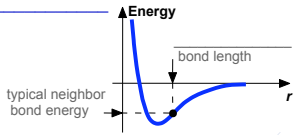
Chapter 3: The Structure of Crystalline Solids

ISSUES TO ADDRESS...

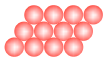
- How do atoms assemble into solid structures?
- How does the density of a material depend on its structure?
- When do material properties vary with the sample (i.e., part) orientation?

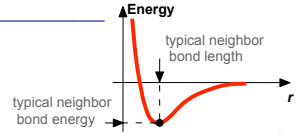
Energy and Packing

- Non dense, _____



- Dense, _____

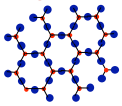




Dense, _____ to have _____ energies.

Materials and Packing

Crystalline materials...
- atoms pack _____, 3D arrays
- typical of: -_____
  -many _____
  -some _____

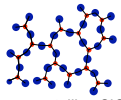


crystalline SiO_2

Adapted from Fig. 3.23(a), *Callister & Rethwisch 8e.*

• Si • Oxygen

Noncrystalline materials...
- atoms have no periodic packing
- occurs for: - _____
  - _____



noncrystalline SiO_2

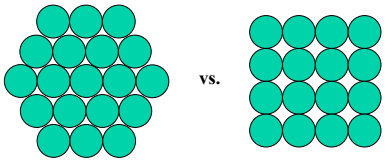
Adapted from Fig. 3.23(b), *Callister & Rethwisch 8e.*

"Amorphous" = Noncrystalline

Metallic Crystal Structures

- How can we stack metal atoms to minimize empty space?

2-dimensions



Now stack these 2-D layers to make 3-D structures

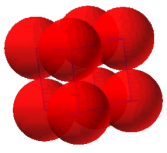
Metallic Crystal Structures

- Tend to be densely packed.
- Reasons for dense packing:
  - Typically, only one _____is present, so all atomic _____ are the same.
  - Metallic bonding is not _____.
  - Nearest neighbor distances tend to be small in order to _____ bond energy.
  - _____ cloud shields cores from each other
- Have the simplest crystal structures.

We will examine three such structures...

Simple Cubic Structure (SC)

- Rare due to low packing density (only Po has this structure)
- Close-packed _____ are cube edges.



Click once on image to start animation
(Courtesy P.M. Anderson)

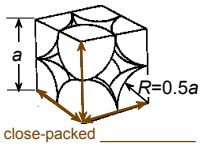
- Coordination # = ___
  (# nearest neighbors)

Atomic Packing Factor (APF)

$$APF = \frac{\text{Volume of atoms in unit cell*}}{\text{Volume of unit cell}}$$

*assume hard spheres

- APF for a simple _____ structure = 0.52



close-packed _____

contains 8 x 1/8 =

1 atom/unit cell

Adapted from Fig. 3.24, *Callister & Rethwisch 8e.*

$$APF = \frac{\text{atoms}}{\text{unit cell}} \cdot \frac{\text{volume}}{\text{atom}} = \frac{1 \cdot \frac{4}{3}\pi (0.5a)^3}{a^3}$$

a^3: volume / unit cell

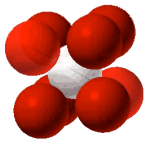
Body Centered Cubic Structure (BCC)

- Atoms touch each other along cube _____.

--Note: All atoms are identical; the center atom is shaded differently only for ease of viewing.

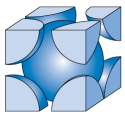
ex: Cr, W, Fe (α), Tantalum, _____

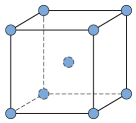
- Coordination # = 8



Click once on image to start animation

(Courtesy P.M. Anderson)



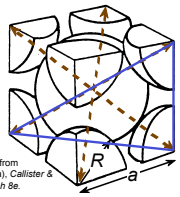


Adapted from Fig. 3.2, *Callister & Rethwisch 8e.*

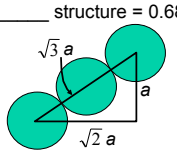
2 atoms/unit cell: 1 center + 8 _____

Atomic Packing Factor: BCC

- APF for a body-centered _____ structure = 0.68



Adapted from Fig. 3.2(a), *Callister & Rethwisch 8e.*



Close-packed _____:

length = $4R = \sqrt{3}\,a$

$$APF = \frac{\text{atoms}}{\text{unit cell}} \cdot \frac{\text{volume}}{\text{atom}} = \frac{2 \cdot \frac{4}{3}\pi (\sqrt{3}a/4)^3}{a^3}$$

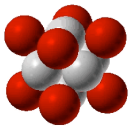
a^3: volume / unit cell

Face Centered Cubic Structure (FCC)

- Atoms touch each other along face _____.
  --Note: All atoms are _____; the face-centered atoms are shaded differently only for ease of viewing.

ex: Al, Cu, Au, Pb, Ni, Pt, Ag

- Coordination # = ___



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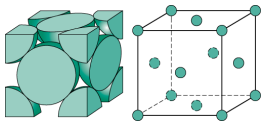
(Courtesy P.M. Anderson)

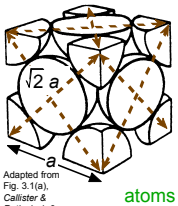


Adapted from Fig. 3.1, *Callister & Rethwisch 8e.*

4 atoms/unit cell: 6 _____ + 8 corners x 1/8

Atomic Packing Factor: FCC

- APF for a face-centered cubic structure = 0.74
  maximum achievable APF



Adapted from Fig. 3.1(a), *Callister & Rethwisch 8e.*

Close-packed directions:
length = $4R = \sqrt{2}\,a$

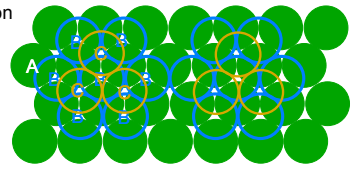
Unit cell contains:

_____
= _____

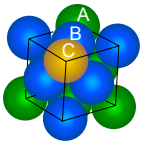
$$\text{APF} = \frac{\text{atoms}}{\text{unit cell}} \cdot \frac{\text{volume}}{\text{atom}} \Big/ \frac{\text{volume}}{\text{unit cell}} = \frac{\frac{4}{3}\pi\left(\frac{\sqrt{2}a}{4}\right)^3}{\text{volume/unit cell}}$$

FCC Stacking Sequence

- ABCABC... _____ Sequence
- 2D Projection

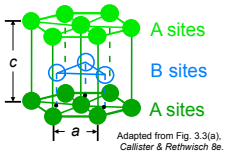


- FCC _____ Cell



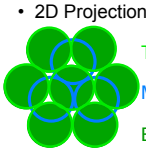
Hexagonal Close-Packed Structure (HCP)

- ABAB... Stacking Sequence
- 3D Projection



Adapted from Fig. 3.3(a), *Callister & Rethwisch 8e.*

- 2D Projection



- Coordination # = ___
- APF = _____
- *c/a* = _____

__ atoms/unit cell

ex: Cd, Mg, Ti, Zn

Theoretical Density, ρ

$$\text{Density} = \rho = \frac{\text{Mass of Atoms in Unit Cell}}{\text{Total Volume of Unit Cell}}$$

$$\rho = \frac{nA}{V_C N_A}$$

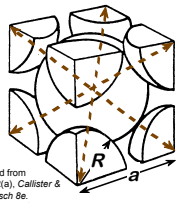
where n = _____

A = atomic weight

V_C = _____ = _____

N_A = Avogadro's number = 6.022×10^{23} atoms/mol

Theoretical Density, ρ



Adapted from Fig. 3.2(a), *Callister & Rethwisch 8e.*

- Ex: Cr (BCC)

A = 52.00 g/mol

R = _____

n = 2 atoms/unit cell

$a = 4R/\sqrt{3} = 0.2887$ nm

$$\rho = \frac{\frac{\text{atoms}}{\text{unit cell}} \times \frac{\text{g}}{\text{mol}}}{\text{volume} \times \frac{\text{atoms}}{\text{mol}}} = \frac{52.00}{a^3 \times 6.022 \times 10^{23}}$$

$\rho_{theoretical}$	= 7.18 g/cm^3
ρ_{actual}	= 7.19 g/cm^3

Densities of Material Classes

In general

$\rho_{metals} > \rho_{ceramics} > \rho_{polymers}$

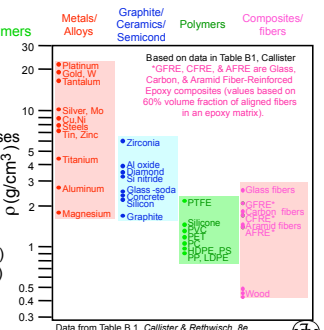
Why?

Metals have...
- close-packing (metallic bonding)
- often _____atomic masses

Ceramics have...
- less _____packing
- often lighter elements

Polymers have...
- low packing _____ (often _____)
- lighter elements (C,H,O)

Composites have...
- _____values



Data from Table B.1, *Callister & Rethwisch, 8e.*

Crystals as Building Blocks

- *Some* engineering applications require _____crystals:
  - -- diamond single crystals for abrasives
  - -- turbine blades

(Courtesy Martin Deakins, GE Superabrasives, Worthington, OH. Used with permission.)

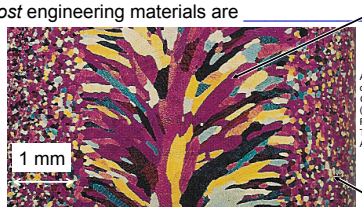
Fig. 8.33(c), *Callister & Rethwisch 8e.* (Fig. 8.33(c) courtesy of Pratt and Whitney).

- Properties of _____materials often related to crystal structure.
  - -- Ex: Quartz fractures more easily along some crystal planes than others.

(Courtesy P.M. Anderson)

Polycrystals

- *Most* engineering materials are _____



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

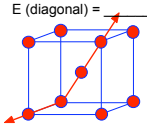
Isotropic

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

Single vs Polycrystals

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

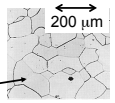
E (diagonal) = _____

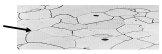


E (edge) = 125 GPa

Data from Table 3.3, *Callister & Rethwisch 8e.* (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 _____ oriented: _____.
    ($E_{poly\ iron}$ = 210 GPa)
  - -If grains are _____, anisotropic.





Adapted from Fig. 4.14(b), *Callister & Rethwisch 8e.* (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].)

Polymorphism

- Two or more distinct _____ structures for the same material (allotropy/polymorphism)

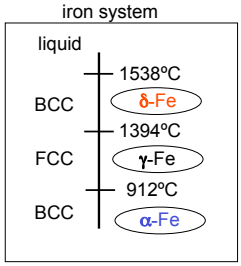
titanium

α, β-Ti

carbon

_____, graphite

iron system



Crystal Systems

Unit cell: smallest _____ which contains the complete _____ of a crystal.

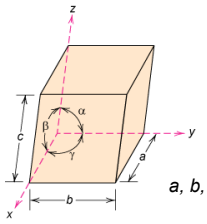


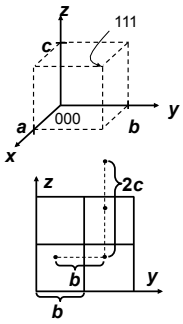
Fig. 3.4, *Callister & Rethwisch 8e.*

7 crystal systems

14 crystal lattices

a, *b*, and *c* are the _____ constants

Point Coordinates



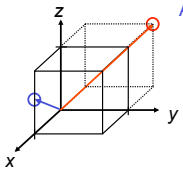
Point coordinates for _____ center are

a/2, *b*/2, *c*/2 ½½½

Point _____ for unit cell corner are 111

_____: integer multiple of lattice constants → identical position in another unit cell

Crystallographic Directions



Algorithm

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

[*uvw*]

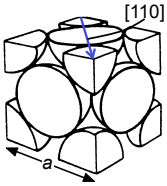
ex: _____

_____ where _____ represents a negative index

_____ of directions <*uvw*>

Linear Density

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



Adapted from Fig. 3.1(a), *Callister & Rethwisch 8e.*

ex: linear _____ of Al in [110] direction

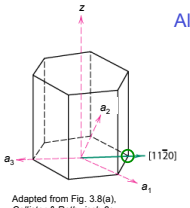
a = 0.405 nm

atoms

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

length

HCP Crystallographic Directions

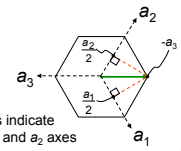


Adapted from Fig. 3.8(a), *Callister & Rethwisch 8e.*

Algorithm

1. Vector _____ (if necessary) to pass through origin.
2. Read off projections in _____ of unit cell dimensions a_1, a_2, a_3, or c
3. Adjust to _____ integer values
4. Enclose in square brackets, no commas

[*uvtw*]



ex: _____

_____ red lines indicate projections onto a_1 and a_2 axes

HCP Crystallographic Directions

- Hexagonal Crystals
  - 4 parameter _____ lattice coordinates are related to the direction _____ (i.e., *u'v'w'*) as follows.

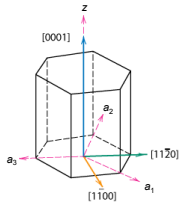


Fig. 3.8(a), *Callister & Rethwisch 8e.*

$$[u'v'w'] \rightarrow [uvtw]$$

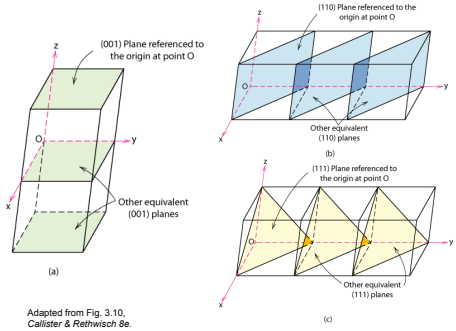
$$u = \frac{1}{3}(2u' - v')$$

$$v = \frac{1}{3}(2v' - u')$$

$$t = -(u + v)$$

$$w = w'$$

Crystallographic Planes



Adapted from Fig. 3.10, *Callister & Rethwisch 8e.*

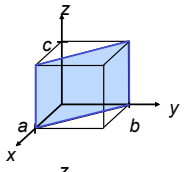
Crystallographic Planes

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

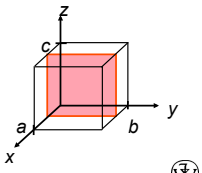
- Algorithm
  1. Read off _____ of plane with axes in terms of *a*, *b*, *c*
  2. Take _____ of intercepts
  3. Reduce to smallest integer values
  4. Enclose in parentheses, no commas i.e., (*hkl*)

Crystallographic Planes

example	*a*	*b*	*c*
1. Intercepts	1	1	___
2. Reciprocals	1/1	1/1	___
	1	1	0
3. Reduction	1	1	___
4. Miller Indices	_____		

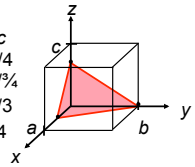


example	*a*	*b*	*c*
1. Intercepts	1/2	∞	∞
2. Reciprocals	1/½	1/∞	1/∞
	2	0	0
3. Reduction	___	___	0
4. Miller Indices	_____		



Crystallographic Planes

example	*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)		



Family of Planes {*hkl*}

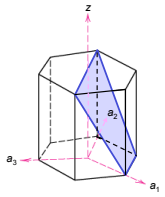
Ex: {100} = (100), (010), (001), ($\bar{1}$00), (0$\bar{1}$0), (00$\bar{1}$)

Crystallographic Planes (HCP)

- In hexagonal unit cells the same idea is used

example	a_1	a_2	a_3	c
1. Intercepts	1	∞	-1	1
2. Reciprocals	1	1/∞	-1	1
	1	0	-1	1
3. Reduction	1	0	-1	1

4. Miller-Bravais Indices $(10\bar{1}1)$



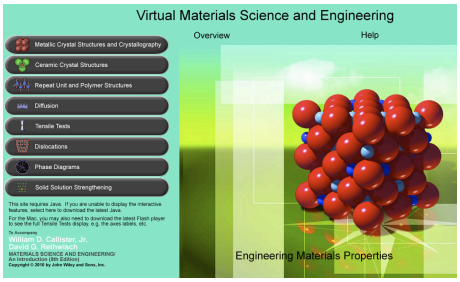
Adapted from Fig. 3.8(b), *Callister & Rethwisch 8e.*

Crystallographic Planes

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

Virtual Materials Science & Engineering (VMSE)

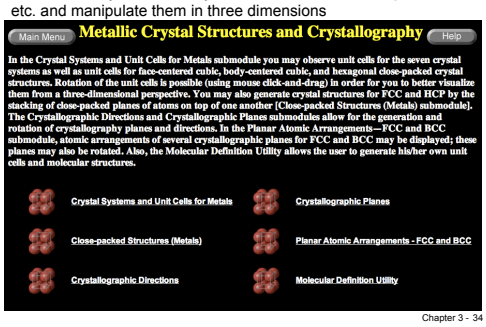
- VMSE is a tool to visualize materials science topics such as crystallography and polymer structures in three dimensions



- Available in Student Companion Site at www.wiley.com/college/callister and in WileyPLUS

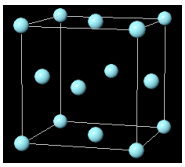
VMSE: Metallic Crystal Structures & Crystallography Module

- VMSE allows you to view crystal structures, directions, planes, etc. and manipulate them in three dimensions

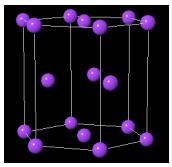


Unit Cells for Metals

- VMSE allows you to view the unit cells and manipulate them in three dimensions
- Below are examples of actual VMSE screen shots

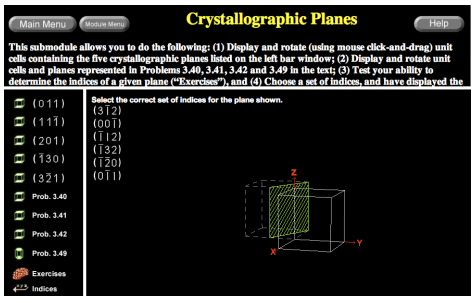


FCC Structure



HCP Structure

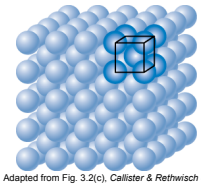
VMSE: Crystallographic Planes Exercises



Additional practice on indexing crystallographic planes

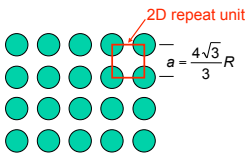
Planar Density of (100) Iron

Solution: At T < 912ºC iron has the _____structure.



Adapted from Fig. 3.2(c), *Callister & Rethwisch 8e.*

(100)



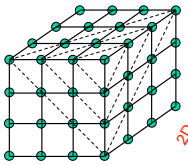
_____of iron $R = 0.1241$ nm

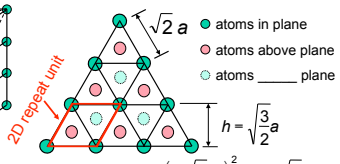
$$\text{Planar Density} = \frac{\frac{\text{atoms}}{\text{2D repeat unit}}}{\frac{\text{area}}{\text{2D repeat unit}}} = \frac{\square}{a^2} = \frac{1}{\left(\frac{4\sqrt{3}}{3}R\right)^2} = \frac{\text{atoms}}{\text{nm}^2} = \frac{\text{atoms}}{\text{m}^2}$$

Planar Density of (111) Iron

Solution (cont): (___) plane

_____ in plane/ unit surface cell



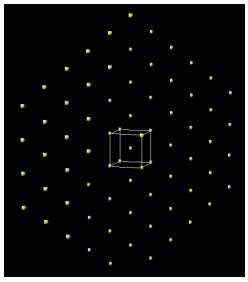


$$\text{area} = \sqrt{2}\,ah = \sqrt{3}\,a^2 = \sqrt{3}\left(\frac{4\sqrt{3}}{3}R\right)^2 = \frac{16\sqrt{3}}{3}R^2$$

$$\text{Planar Density} = \frac{\frac{\text{atoms}}{\text{2D repeat unit}}}{\frac{\text{area}}{\text{2D repeat unit}}} = \frac{\square}{\frac{16\sqrt{3}}{3}R^2} = 7.0\frac{\text{atoms}}{\text{nm}^2} = \frac{\text{atoms}}{\text{m}^2}$$

VMSE Planar Atomic Arrangements

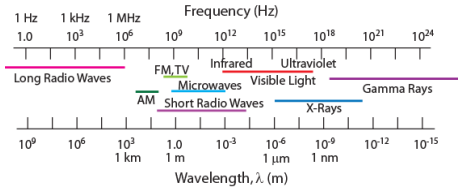
- VMSE allows you to view planar arrangements and rotate them in 3 dimensions



BCC (110) Plane

X-Ray Diffraction

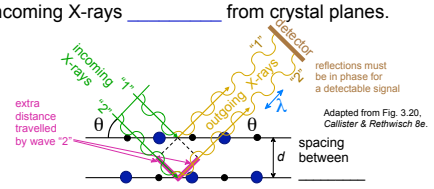
Electromagnetic Spectrum



- _____ gratings must have spacings comparable to the wavelength of diffracted _____.
- Can't resolve _____ < λ
- Spacing is the distance between _____ planes of atoms.

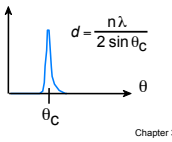
X-Rays to Determine Crystal Structure

- Incoming X-rays _____ from crystal planes.

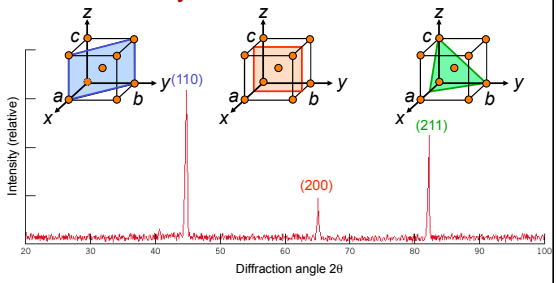


_____of critical angle, θ_c, allows computation of planar _____, *d*.

X-ray intensity (from detector)



X-Ray Diffraction Pattern



Diffraction pattern for polycrystalline α-iron (BCC)

Adapted from Fig. 3.22, *Callister 8e.*

SUMMARY

- Atoms may assemble into crystalline or amorphous structures.
- Common metallic crystal structures are FCC, BCC, and HCP. Coordination number and atomic packing factor are the same for both FCC and HCP crystal structures.
- We can predict the density of a material, provided we know the atomic weight, atomic radius, and crystal geometry (e.g., FCC, BCC, HCP).
- Crystallographic points, directions and planes are specified in terms of indexing schemes. Crystallographic directions and planes are related to atomic linear densities and planar densities.

SUMMARY

- Materials can be single crystals or polycrystalline. Material properties generally vary with single crystal orientation (i.e., they are anisotropic), but are generally non-directional (i.e., they are isotropic) in polycrystals with randomly oriented grains.
- Some materials can have more than one crystal structure. This is referred to as polymorphism (or allotropy).
- X-ray diffraction is used for crystal structure and interplanar spacing determinations.