

Chem 584: Structure of Solids Outline

- The lattice and unit cells
- Describing lines and planes in crystals
- The reciprocal lattice
- Symmetry
- Crystal Systems
- Lattice centering and Bravais lattices
- Indexing in the hexagonal crystal system
- Crystal structures and fractional coordinates
- Crystal habit (shape)
- Stacking faults and twins
- Introduction to the stereographic projection

Textbooks: Solid State Chemistry

1. Shriver, Atkins, *Inorganic Chemistry*
W.H. Freeman and Company (Chs. 2, 18 ...)
2. A.R. West, *Basic Solid State Chemistry (2nd ed. 1999)*
Wiley, New York, 1999

Describing condensed phase structures

- Describing the structure of an isolated small molecule is easy to do
 - Just specify the bond distances and angles
- How do we describe the structure of a condensed phase?
 - we have ~ Avogadro's number of atoms to locate
 - we should either give up on specifying the position of every atom or find a trick to help us out

Frequently used classifications for solids

amorphous solids (short distance order only, e.g. glasses...): special physical and chemical properties ...

crystalline solids (long distance order): synthesis and crystal growth, defects, structure – chemical bonding – physical properties ...

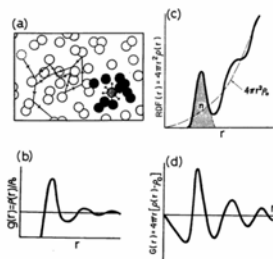
covalent solids (e.g. diamond, boron nitride): extreme hardness, very high melting points ...

ionic solids (e.g. NaCl): structural chemistry, ionic conductivity ...

metals, semiconductors, insulators (different electrical conductivity): close packings of spheres, alloys, mechanical and electrical properties, chemical bonding ...

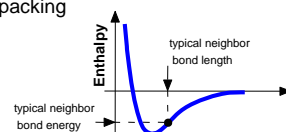
The structure of liquids and glasses

- We can use pair distribution functions to describe the structure of such systems

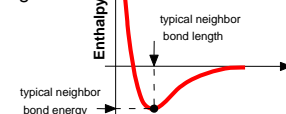
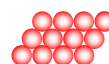


Energy and Packing

- Non-dense, **random** packing



- Dense, **ordered** packing

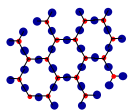


Dense, ordered packed structures tend to have lower enthalpies, but entropy goes favors less ordered packing.

Materials and Packing

Crystalline materials...

- atoms pack in periodic, 3D arrays
- typical of:
 - metals
 - many ceramics
 - some polymers

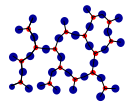


crystalline SiO₂
Adapted from Fig. 3.22(a), Callister 7e.

• Si • Oxygen

Noncrystalline materials...

- atoms have no periodic packing
- occurs for:
 - complex structures
 - rapid cooling



noncrystalline SiO₂
Adapted from Fig. 3.22(b), Callister 7e.

"Amorphous" = Noncrystalline

Crystals

- Crystals are materials with a regular internal structure
- They have internal translational symmetry
 - Some structural motif is repeated at regular intervals throughout the solid
- Just because a material has nice flat faces it is not necessarily a crystal
 - Cut "crystal" glass is not a crystal!
- Not all crystals have well developed faces

The structure of crystalline materials

- We can use the symmetry of a crystal to reduce the number of unique atom positions we have to specify
- The most important type of symmetry is translational
 - this can be described by a lattice
 - A lattice is just a series of points describing the translational symmetry of solid
 - The lattice points do not represent individual atoms!!
- The structure associated with the lattice can be carved up into boxes (unit cells) that pack together to reproduce the whole crystal structure

Crystal Systems

Unit cell: smallest repetitive volume which contains the complete lattice pattern of a crystal.

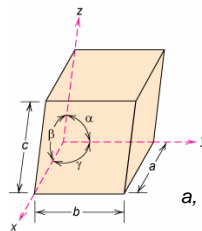


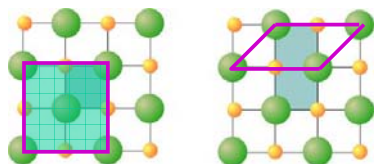
Fig. 3.4, Callister 7e.

7 crystal systems

14 crystal lattices

a , b , and c are the lattice constants

Unit Cells and Coordination Numbers



Unit Cell: An "imaginary" parallel sided region of a structure from which the entire crystal can be constructed by purely translational displacements (Contents of unit cell represents chemical composition)

Space Lattice: A pattern that is formed by the points that represent the locations of the atoms (molecules).

Coordination Number (CN): Number of direct neighbours of a given atom ("first coordination sphere")

The lattice and unit cell in 1D

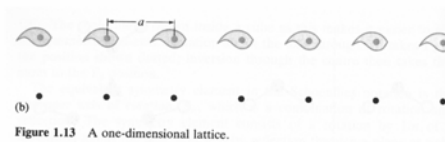
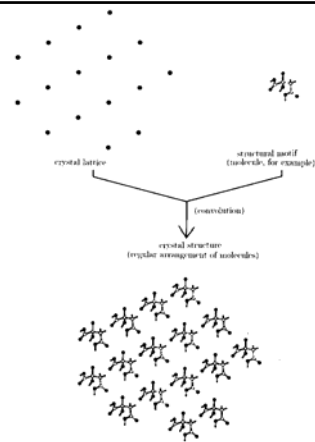


Figure 1.13 A one-dimensional lattice.

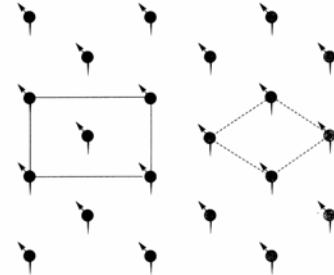


Figure 1.15 Choice of unit cell in a one-dimensional lattice.

The Lattice



Unit cell choice in 2D



Unit cell choice in 2D

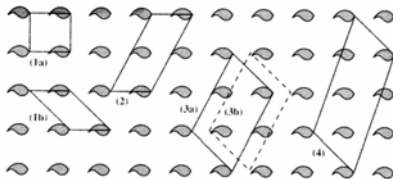


Figure 1.16 Choice of unit cells in a square two-dimensional lattice.



Figure 1.17 Choice of unit cell in a centred rectangular lattice.

Lattices and unit cells 2 D

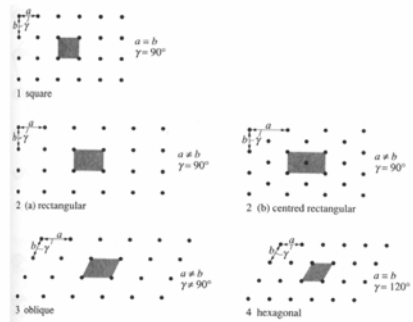
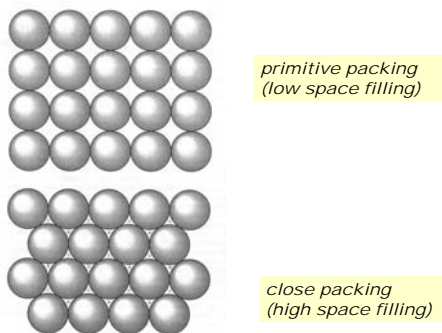


Figure 1.14 The five two-dimensional lattices.

Two-dimensional packing of spheres (atoms)



Metallic Crystal Structures

- **Tend to be densely packed.**
- **Reasons for dense packing:**
Typically, only one element is present, so all atomic radii are equal. Metallic bonding is not directional. Nearest neighbor distances tend to be small. Electron cloud shields cores from each other (non-local bonding)

- **Have the simplest crystal structures.**

We will examine four such structures:

simple cubic (SC),
body centered cubic (BCC),
face centered cubic = cubic close packed (FCC=CCP),
hexagonal close packed (HCP)

Simple Cubic Structure (SC)

- Rare due to low packing density (only Po has this structure)
- Only the cube edges are close-packed directions.

Coordination # = 6
(# nearest neighbors)

Atomic Packing Factor (APF): Simple Cubic

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

*assume hard spheres

- APF for a simple cubic structure = 0.52

$$\text{APF} = \frac{1 \cdot \frac{4}{3} \pi (0.5a)^3}{a^3}$$

close-packed directions contains $8 \times 1/8 = 1$ atom/unit cell

Body Centered Cubic Structure (BCC)

- Atoms touch each other along cube diagonals.

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

ex: Cr, W, Fe (α), Tantalum, Molybdenum

- Coordination # = 8

2 atoms/unit cell: 1 center + 8 corners $\times 1/8$

(Courtesy P.M. Anderson)

Atomic Packing Factor: BCC

- APF for a body-centered cubic structure = 0.68

$$\text{APF} = \frac{2 \cdot \frac{4}{3} \pi (\sqrt{3}a/4)^3}{a^3}$$

Close-packed directions: length = $4R = \sqrt{3}a$

Adapted from Fig. 3.2(a), Callister 7e.

Three-dimensional packing of spheres (atoms)

hexagonal close packing (hcp) vs. cubic close packing (ccp=fcc)

ABAB:
hexagonal close packing (hcp)

ABCABC:
cubic close packing (ccp) = face centered cubic (fcc)

Close-packed planes
2-D hexagonal symmetry

Close-Packed Structures

- HCP from stacking of close-packed planes:
A B A B A B ...

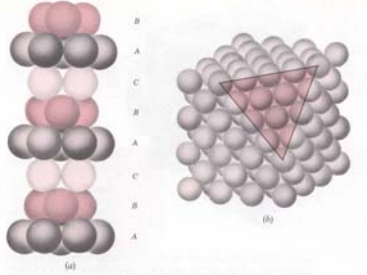
Hex_cp.mov


Movie from "Visualizations in Materials Science," Prof. John C. Russ, North Carolina State University

Close-Packed Structures

- CCP/FCC from stacking of close-packed planes: **A B C A B C ...**

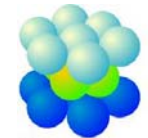
Movie from "Visualizations in Materials Science," Prof. John C. Russ, North Carolina State University





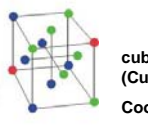
Hex_fcc.mov

Common unit cells for hcp and ccp(=fcc)



(a)

hexagonal close packing (hcp)
(Be, Mg, Zn, Cd, Ti, Zr, Ru ...)
Coordination # = 12

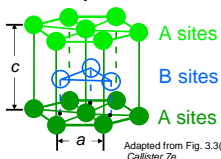


(b)

cubic close packing (ccp or fcc)
(Cu, Ag, Au, Al, Ni, Pd, Pt ...)
Coordination # = 12

Hexagonal Close-Packed Structure (HCP)


- ABAB... Stacking Sequence
- 3D Projection
- 2D Projection



A sites
B sites
A sites

c
 a

Adapted from Fig. 3.3(a), Callister 7e.



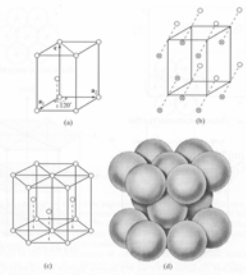
Top layer
Middle layer
Bottom layer

6 atoms/unit cell
ex: Cd, Mg, Ti, Zn

- Coordination # = 12
- APF = 0.74
- $c/a = 1.633$

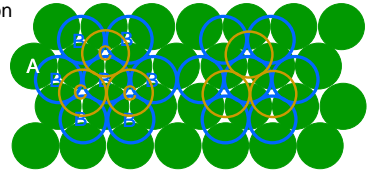
Hexagonal close packing

- Each lattice point is associated with two atoms. One at the corner of the unit cell and one inside the unit cell
- Note this structure is an ABABAB... repeat of closepacked layers

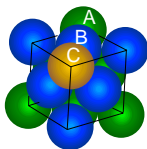


FCC Stacking Sequence

- ABCABC... Stacking Sequence
- 2D Projection



A sites
B sites
C sites



A
B
C


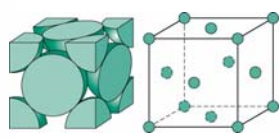
- FCC Unit Cell

Face Centered Cubic Structure (FCC)

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

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

- Coordination # = 12

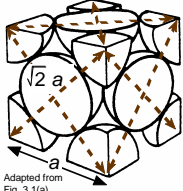
Adapted from Fig. 3.1, Callister 7e.

4 atoms/unit cell: 6 face x 1/2 + 8 corners x 1/8

(Courtesy P.M. Anderson)

Atomic Packing Factor: FCC

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



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

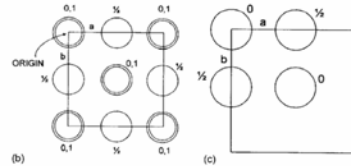
Unit cell contains:
 $6 \times 1/2 + 8 \times 1/8$
= 4 atoms/unit cell

Adapted from
Fig. 3.1(a),
Callister 7e.

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

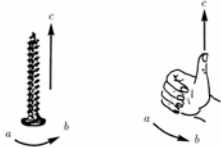
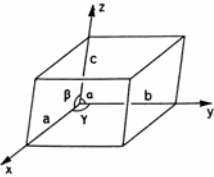
Atomic positions in FCC structure

- Can represent atoms on unit cell projection drawing with heights marked
- Can also give atomic coordinates
 - 0,0,0 0,1/2,1/2 1/2,1/2,0 1/2,0,1/2
 - Only need to specify these four atoms as others are produced by unit cell translational symmetry



The Unit Cell in 3 Dimensions

- Always use a right handed axis system
- Axis lengths are specified by a, b and c
- Interaxial angles are specified by α , β and γ



Lattice and unit cell in 3D

- We specify the lattice using the vectors **a**, **b** and **c**.
 - The vector between any two lattice points (**r**) satisfies the relationship, $\mathbf{r} = n\mathbf{a} + p\mathbf{b} + q\mathbf{c}$, where n, p and q are integers
- There is no fixed relationship between the positions of a unit cell and the lattice that is associated with it
 - The lattice only places constraints on the size and shape of the unit cell, not position

Picking a unit cell for NaCl

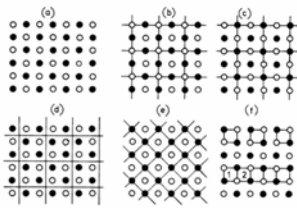


Fig. 1.1 (a) Section through the NaCl structure, showing (b) to (g) possible repeat units, and (h) incorrect units

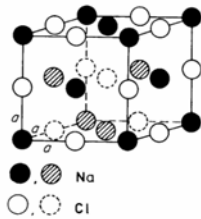


Fig. 1.2 Cubic unit cell of NaCl, $a = b = c$

Unit cell choice

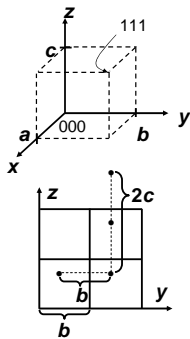
- There is always more than possible choice of unit cell
- By convention the unit cell is chosen so that it is as small as possible while reflecting the full symmetry of the lattice
- If the unit cell contains only one lattice point is said to be primitive. If it contains more than one lattice point it is centered
- There are seven distinct “shapes” of unit cell, that are referred to as the seven crystal systems

Specifying points in crystals

- Frequently need to specify the position of a point, the direction of a line or the orientation of a plane in a crystal
- Can specify a point using
 - $\mathbf{r} = (n+u)\mathbf{a} + (p+v)\mathbf{b} + (q+w)\mathbf{c}$ n, p, q integers
 - $\mathbf{r} = (na + pb + qc) + (ua + vb + wc)$
 - u, v, w are fractional coordinates specifying a position within a unit cell. All positions with the same u, v and w are symmetry equivalent

Chem 584 Structure of Solids, #2

Point Coordinates

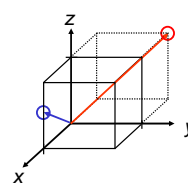


Point coordinates for unit cell center are $a/2, b/2, c/2$ $\frac{1}{2}\frac{1}{2}\frac{1}{2}$

Point coordinates for unit cell corner are 111

Translation: integer multiple of lattice constants \rightarrow identical position in another unit cell

Crystallographic Directions



Algorithm

- Vector repositioned (if necessary) to pass through origin.
- Read off projections in terms of unit cell dimensions $a, b,$ and c
- Adjust to smallest integer values
- Enclose in square brackets, no commas $[uvw]$

ex: $1, 0, \frac{1}{2} \Rightarrow 2, 0, 1 \Rightarrow [201]$

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

families of directions $\langle uvw \rangle$

Miller indices (hkl)

Miller Indices are the reciprocal intercepts of the plane on the unit cell axes

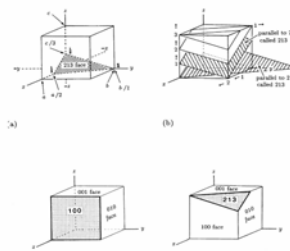
Identify plane adjacent to origin

- can not determine for plane passing through origin

Find intersection of plane on all three axes

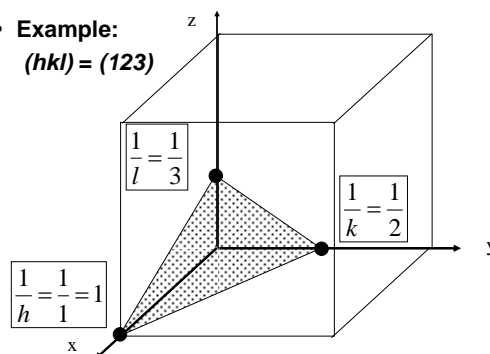
Take reciprocal of intercepts

If plane runs parallel to axis, intercept is at ∞ , so Miller index is 0



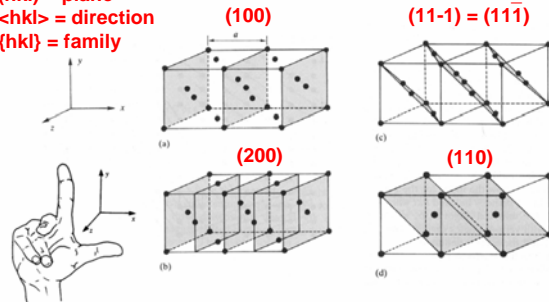
Miller Indices & Crystallographic Planes

- Example:
 $(hkl) = (123)$

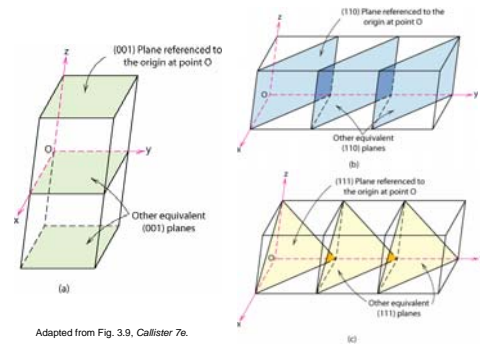


Examples of Miller indices

(hkl) = plane
 $\langle hkl \rangle$ = direction
 $\{hkl\}$ = family



Crystallographic Planes

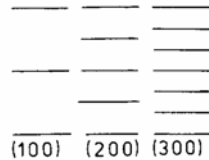


Adapted from Fig. 3.9, Callister 7e.

Families of planes

- Miller indices describe the orientation and spacing of a family of planes
 - The spacing between adjacent planes in a family is referred to as the “d-spacing”

Three different families of planes
 d-spacing between (300) planes is one third of the (100) spacing



Note all (100) planes are members of the (300) family

Crystallographic Planes

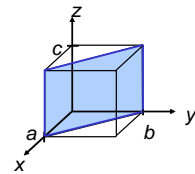
- Miller Indices: Reciprocals of the (three) axial intercepts for a plane, cleared of fractions & common multiples. All parallel planes have same Miller indices.**
- Algorithm**
 - Read off intercepts of plane with axes in terms of a, b, c
 - Take reciprocals of intercepts
 - Reduce to smallest integer values
 - Enclose in parentheses, no commas i.e., (hkl)

Planes of a form

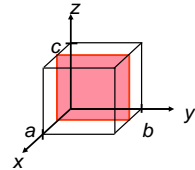
- The symbol $\{hkl\}$ refers to all planes that are symmetry equivalent to (hkl) . This group of equivalent planes are referred to as planes of a form.
- For the cubic system all the planes (100) , (010) , (001) , (-100) , $(0-10)$ and $(00-1)$ belong to the form $\{100\}$
- For a tetragonal material $a=b \neq c$ the form $\{100\}$ would only include (100) , (010) , (-100) , and $(0-10)$

Crystallographic Planes

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



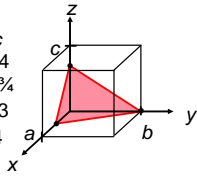
example	a	b	c
1. Intercepts	1/2	∞	∞
2. Reciprocals	1/1/2	1/ ∞	1/ ∞
	2	0	0
3. Reduction	2	0	0
4. Miller Indices	(100)		



Crystallographic Planes

example

	a	b	c
1. Intercepts	1/2	1	3/4
2. Reciprocals	1/1/2	1/1	1/3/4
3. Reduction	2	1	4/3
4. Miller Indices	(634)		



Family of Planes $\{hkl\}$

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

Specifying the direction of a line

- The direction of any line can be specified by drawing a line parallel to the one of interest so that it goes through the unit cell origin and picking any point u', v', w' on the line
 - Conventionally, u', v', w' are multiplied by the smallest number that produces integers u, v, w
- Denote direction of line using the symbol $[uvw]$
 - $[uvw]$ are the indices of the line's direction
 - The use of a square bracket implies that we are talking about a direction
- The notation $\langle uvw \rangle$ implies that we are talking about all directions in a crystal that are symmetry equivalent to $[uvw]$
 - For example, in a cubic material all the body diagonals of the cube are symmetry equivalent. So all the directions $[111], [-111], [1-11], [11-1], [-1-11], [-11-1], [1-1-1]$ and $[-1-1-1]$ are symmetry equivalent. All of them are directions of the form $\langle 111 \rangle$.
 - NOTE typically negative indices are specified using a 'bar' over the number not by a negative sign

d-spacing formulae

- For a unit cell with orthogonal axes
 - $(1/d_{hkl}^2) = (h^2/a^2) + (k^2/b^2) + (l^2/c^2)$
- Hexagonal unit cells
 - $(1/d_{hkl}^2) = (4/3)[(h^2 + k^2 + hk)/a^2] + (l^2/c^2)$

Unit cells and d_{hkl}

TABLE 3.1. Obtaining unit cell dimensions from d_{hkl} values.

The general equation for the spacings between lattice planes d_{hkl} for a crystal with unit-cell dimensions $a, b, c, \alpha, \beta, \gamma$ is given by:

$$d_{hkl} = X/Y,$$

where X and Y are:

$$X = [1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma]^{\frac{1}{2}}$$

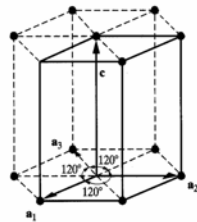
$$Y = \left[\left(\frac{h}{a}\right)^2 \sin^2 \alpha + \left(\frac{k}{b}\right)^2 \sin^2 \beta + \left(\frac{l}{c}\right)^2 \sin^2 \gamma \right. \\ \left. - \frac{2hk}{bc} (\cos \alpha - \cos \beta \cos \gamma) - \frac{2hl}{ca} (\cos \beta - \cos \gamma \cos \alpha) \right. \\ \left. - \frac{2hk}{ab} (\cos \gamma - \cos \alpha \cos \beta) \right]^{\frac{1}{2}} \quad (3.1.1)$$

In systems of higher symmetry, this equation is greatly simplified. For example, if $\alpha = \beta = \gamma = 90^\circ$:

$$d_{hkl} = 1 / \sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}} \quad (3.1.2)$$

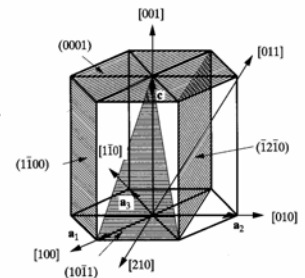
Indexing in the hexagonal system

- In hexagonal unit cells it is common to refer the orientation of planes and lines to four coordinate axes
 - The fourth axis a_3 is just $= -a_2 - a_1$. This approach reflects the three fold symmetry associated with the unit cell

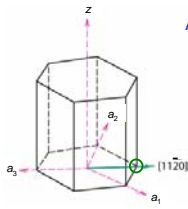


Properties of hexagonal indices

- Indices are expressed as $(hkil)$
 - $h + k = -i$
 - All cyclic permutations of h, k and i are symmetry equivalent
 - So $(10-10), (-1100), (0-110)$ are equivalent



HCP Crystallographic Directions



Algorithm

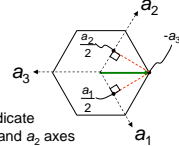
1. Vector repositioned (if necessary) to pass through origin.
2. Read off projections in terms of unit cell dimensions a_1 , a_2 , a_3 , or c
3. Adjust to smallest integer values
4. Enclose in square brackets, no commas

$[uvw]$

ex: $\frac{1}{2}, \frac{1}{2}, -1, 0$

$\Rightarrow [11\bar{2}0]$

dashed red lines indicate projections onto a_1 and a_2 axes



HCP Crystallographic Directions

Hexagonal Crystals

4 parameter Miller-Bravais lattice coordinates are related to the direction indices (i.e., $u'v'w'$) as follows.

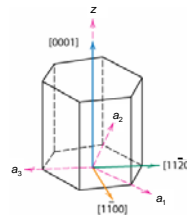


Fig. 3.8(a), Callister 7e.

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

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

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

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

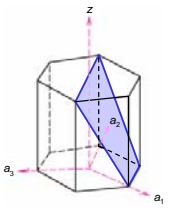
$$w = w'$$

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	$1/\infty$	-1	1
3. Reduction	1	0	-1	1
4. Miller-Bravais Indices	$(10\bar{1}1)$			

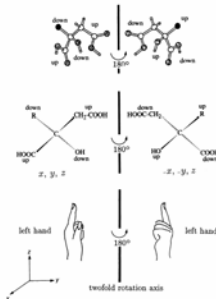


Adapted from Fig. 3.8(a), Callister 7e.

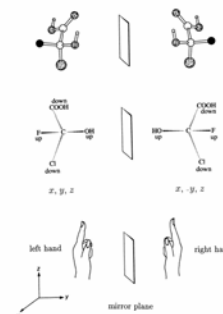
Point symmetry elements

- In addition to the translational symmetry associated with a lattice, most materials have addition point symmetry
- Point symmetry elements operate to change the orientation of structural motifs
- A point symmetry operation does not alter at least one point that it operates on
- Point symmetry elements include
 - rotation axes
 - mirror planes
 - rotation-inversion axes

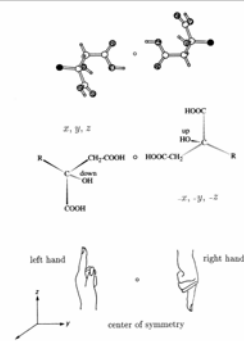
A two fold rotation



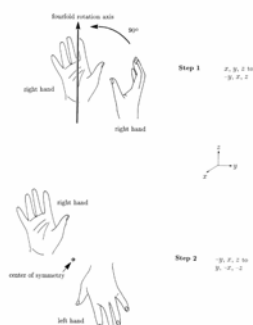
A mirror plane



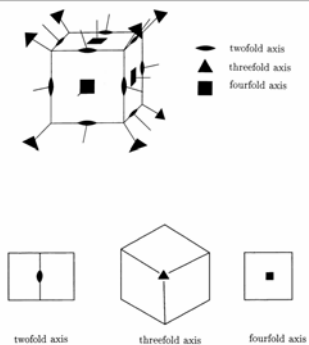
An inversion center



A rotation inversion axis



The symmetry elements of a cube



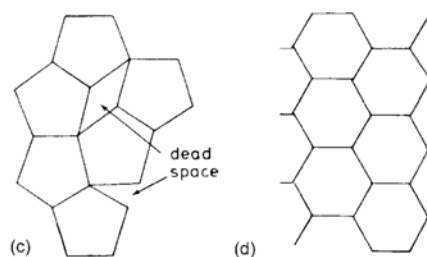
All combinations of point symmetry elements are not possible

- A three fold axis can not just have one two fold axis perpendicular to it
- In three dimensions the existence of two perpendicular two folds implies the existence of a third perpendicular two fold
- The allowed combinations of point symmetry elements are called point groups

Point symmetry elements compatible with 3D translations

Symmetry element	Symbol
Mirror plane	m
Rotation axis	$n = 2, 3, 4, 6$
Inversion axis	$n (= 1, 2, 3, 4, 6)$
Center of symmetry	i

Point symmetry and packing



The 32 point groups

Only 32 point groups are consistent with periodicity in 3D

Schönflies and Hermann-Mauguin symbols for crystallographic point groups

- Rotation axes ($C^n = \text{cyclic}$):

C_1	1	C_4	4
C_2	2	C_3	6
C_6	3		
- Rotation axes plus plane of symmetry normal to those axes ($\sigma = \text{Sphæropentag}$):

C_2^h	cn	C_2^v	$4/m$
C_3^h	$3/m$	C_2^v	$6/m$
C_6^h	$3/m = \bar{6}$		
- Plane of symmetry through an axis:

C_2^v	$nm2$	C_2^v	$4mm$
C_3^v	$3m$	C_2^v	$6mm$
- Rotatory-inversion axes ($S = \text{Sphæroinvers}$):

$S_2 = C_2$	$\bar{1}$	$S_4 = C_4^2$	$\bar{3}$
S_6	$\bar{6}$		
- Rotation axis, degree n , with a twofold axis normal to it ($D = \text{Diedergruppe}$):

$D_2 = C_2$	222	D_4	422
D_3	32	D_6	622
- Rotation axis with twofold axes normal to it plus a horizontal plane:

$D_2^h = C_2$	$2/m$	D_4^h	$4/m$
D_3^h	$3/m$	D_6^h	$6/m$
- D group with additional diagonal in the vertical plane:

D_2^d	$2/m$	D_4^d	$4/m$
D_3^d	$3/m$	D_6^d	$6/m$
- Cubic group ($T = \text{tetrahedral}$, $O = \text{octahedral}$):

T	23	T_d	$\bar{24}$
T_h	$m\bar{3}$	O	48
O_h	$m\bar{3}2$	O_h	$m\bar{3}2$

Symbols for symmetry elements 1

Symmetry axis or symmetry point	Graphical symbol*	Screw vector of a right-handed screw rotation in units of the shortest lattice translation vector parallel to the axis	Printed symbol (subelements in parentheses)
Identity	None	None	1
Twofold rotation axis	\updownarrow	None	2
Twofold rotation point (two dimensions)	\updownarrow	$\frac{1}{2}$	2_1
Twofold screw axis: '2 sub 1'	\updownarrow	$\frac{1}{2}$	2
Threefold rotation axis	\blacktriangle	None	3
Threefold rotation point (two dimensions)	\blacktriangle	$\frac{1}{3}$	3_1
Threefold screw axis: '3 sub 1'	\blacktriangle	$\frac{1}{3}$	3_2
Threefold screw axis: '3 sub 2'	\blacktriangle	$\frac{2}{3}$	3
Fourfold rotation axis	\blacklozenge	None	4 (2)
Fourfold rotation point (two dimensions)	\blacklozenge	$\frac{1}{4}$	4_1 (2)
Fourfold screw axis: '4 sub 1'	\blacklozenge	$\frac{1}{4}$	4_2 (2)
Fourfold screw axis: '4 sub 2'	\blacklozenge	$\frac{2}{4}$	4_1 (2)
Fourfold screw axis: '4 sub 3'	\blacklozenge	$\frac{3}{4}$	4 (2)
Sixfold rotation axis	\bullet	None	6 (3,2)
Sixfold rotation point (two dimensions)	\bullet	$\frac{1}{6}$	6 (3,2)
	∞		

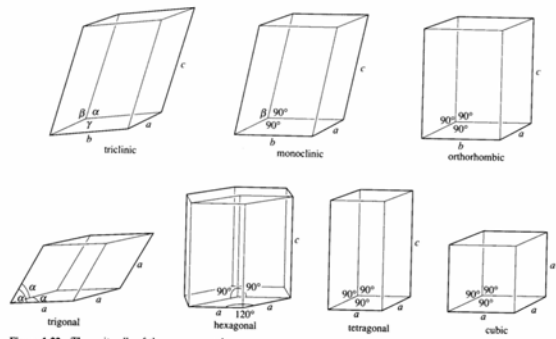
Symbols for symmetry elements 2

Sixfold screw axis: '6 sub 1'	\updownarrow	$\frac{1}{6}$	6_1 (3,2)
Sixfold screw axis: '6 sub 2'	\updownarrow	$\frac{2}{6}$	6_2 (3,2)
Sixfold screw axis: '6 sub 3'	\updownarrow	$\frac{3}{6}$	6_3 (3,2)
Sixfold screw axis: '6 sub 4'	\updownarrow	$\frac{4}{6}$	6_4 (3,2)
Sixfold screw axis: '6 sub 5'	\updownarrow	$\frac{5}{6}$	6_5 (3,2)
Centre of symmetry, inversion centre: '1 bar'	\circ	None	$\bar{1}$
Reflection point, mirror point (one dimension)	σ		
Inversion axis: '3 bar'	\blacktriangle	None	$\bar{3}$ (3,1)
Inversion axis: '4 bar'	\blacktriangle	None	$\bar{4}$ (2)
Inversion axis: '6 bar'	\blacktriangle	None	$\bar{6}$ (3/m)
Twofold rotation axis with centre of symmetry	\updownarrow	None	$2/m$ (1)
Twofold screw axis with centre of symmetry	\updownarrow	$\frac{1}{2}$	$2_1/m$ (1)
Fourfold rotation axis with centre of symmetry	\updownarrow	None	$4/m$ (4,2,1)
'4 sub 2' screw axis with centre of symmetry	\updownarrow	$\frac{1}{2}$	$4_2/m$ (4,2,1)
Sixfold rotation axis with centre of symmetry	\updownarrow	None	$6/m$ (6,3,3,2,1)
'6 sub 3' screw axis with centre of symmetry	\updownarrow	$\frac{1}{2}$	$6_3/m$ (6,3,3,2,1)

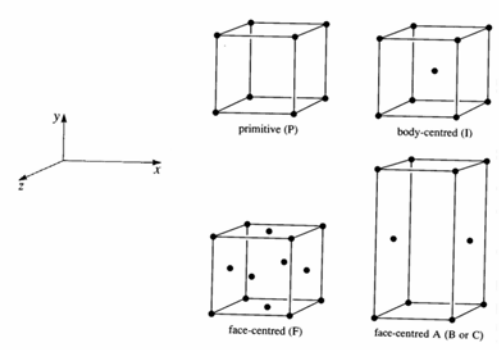
The seven crystal systems

System	Unit Cell	Minimum Symmetry
Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$	None
Monoclinic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	One two-fold axis or one symmetry plane
Orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	Any combination of three mutually perpendicular two-fold axes or planes of symmetry
Trigonal	$a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$	One three-fold axis
Hexagonal	$a = b \neq c$ $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	One six-fold axis or one six-fold improper axis
Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	One four-fold axis or one four-fold improper-axis
Cubic	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	Four three-fold axes at $109^\circ 28'$ to each other

Unit cells in 3D



Centering



Centering operators

- The location of the additional lattice points within the unit cell is described by a set of centering operators
 - Body centered (I) has additional lattice point at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$
 - Face centered (F) has additional lattice points at $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$, and $\frac{1}{2}\frac{1}{2}0$
 - Side centered (C) has an additional lattice point at $\frac{1}{2}\frac{1}{2}0$

Centering 3

- Not all centering possibilities occur for each of the seven crystal systems
 - Only 14 unique combinations (Bravais lattices)
 - Some centering types are not allowed because they would lower the symmetry of the unit cell
 - » E.g side centered cubic is not possible as this would destroy the three fold symmetry that is an essential component of cubic symmetry
 - Some centering types are redundant
 - » C-centered tetragonal can always be described using a smaller primitive tetragonal cell

Bravais Lattices

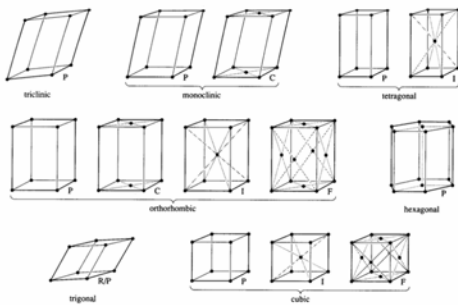


Figure 1.24 The 14 Bravais lattices.

Combining symmetry elements

- For three dimensions
 - 32 point groups
 - 14 Bravais lattices
 - but only 230 space groups
- For two dimensions
 - 5 lattices
 - 10 point groups
 - but only 17 plane groups

Describing crystal structures

- The location of all the atoms in a crystalline solid can be specified by a combination of all the symmetry elements that are appropriate and the fractional coordinates for a unique set of atoms (asymmetric unit)
- Full symmetry of a crystal is described by its space group
- We specify atomic coordinates for a small number of atoms. We then apply all the symmetry elements including the lattice symmetry to build up the full 3D structure.
 - Note each lattice point may be associated with many atoms

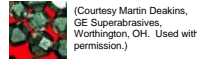
Crystal shape

- ◆ The external shape of a crystal is referred to as its Habit
- ◆ Not all crystals have well defined external faces
 - Typically see faces on crystals grown from solution
- ◆ Natural faces always have low indices (orientation can be described by Miller indices that are small integers)
 - Law of rational indices
- ◆ The faces that you see are the lowest energy faces
 - Surface energy is minimized during growth

Chem 584 Structure of Solids, #3

Crystals as Building Blocks

- Some engineering applications require single crystals: diamond single crystals as abrasives turbine Ti blades



- Properties of crystalline 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 polycrystals.



Anisotropic

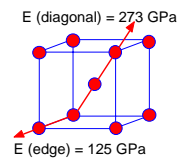
Isotropic

- 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).

Single vs Polycrystals

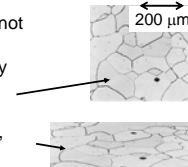
- Single Crystals

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



- Polycrystals

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

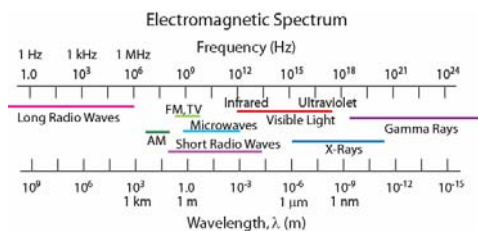


Polymorphism

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

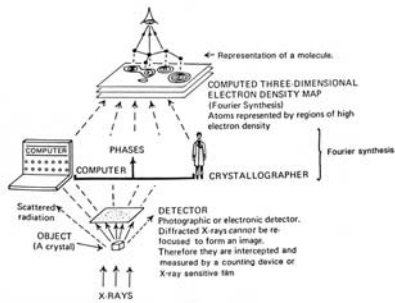
titanium	iron system
α, β-Ti	liquid
	1538°C
	BCC (δ-Fe)
	1394°C
	FCC (γ-Fe)
	912°C
	BCC (α-Fe)
carbon	
diamond, graphite	

X-Ray Diffraction



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

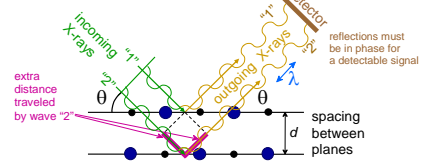
X-ray structure analysis with powders or single crystals



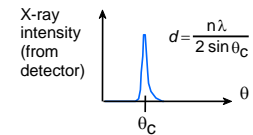
Powder: sample of very small crystals (~ μm)
Single crystal: small crystal (~ mm)
 Physical background: Bragg's law

X-Rays to Determine Crystal Structure

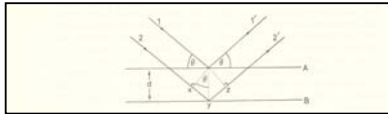
- Incoming X-rays **diffract** from crystal planes.



Measurement of critical angle, θ_c , allows computation of planar spacing, d .



Derivation of Bragg's law for X-Ray diffraction



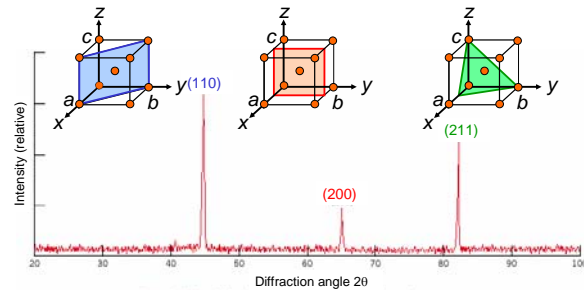
$$xy = yz = d \sin \theta \rightarrow xyz = 2d \sin \theta$$

constructive or destructive interference of X-Ray beams 1 and 2
 If the optical path difference is an **even** or **odd** multiple of $\lambda/2$:

constructive: $2 \times \lambda/2, 4 \times \lambda/2, 6 \times \lambda/2, \dots, n = 1 \times \lambda, 2 \times \lambda, 3 \times \lambda, \dots$
destructive: $1 \times \lambda/2, 3 \times \lambda/2, 5 \times \lambda/2, \dots$

Condition for constructive interference (reflection):
 $n \lambda = 2d \sin \theta$ (Bragg's law)

X-Ray Diffraction Pattern



Diffraction pattern for polycrystalline α -iron (BCC)

Adapted from Fig. 3.20, Callister 5e.

The reciprocal lattice

- It is convenient when talking about diffraction to use the concept of a reciprocal lattice
- The reciprocal lattice is related to the real space lattice by:

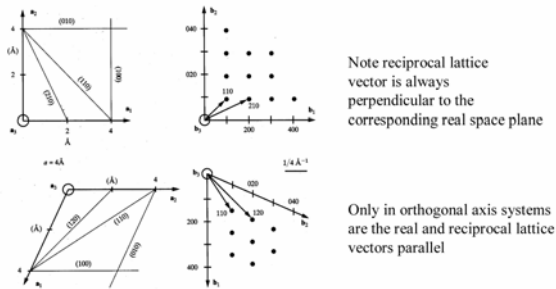
$$b_1 = \frac{a_2 \times a_3}{a_1 \cdot a_2 \times a_3} \quad b_2 = \frac{a_3 \times a_1}{a_1 \cdot a_2 \times a_3} \quad b_3 = \frac{a_1 \times a_2}{a_1 \cdot a_2 \times a_3}$$

- $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ are the vectors of the real space lattice (alternatively $\mathbf{a}, \mathbf{b}, \mathbf{c}$) and $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ are the vectors of the reciprocal lattice (alternatively $\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$).
- Note $a_1 \cdot a_2 \times a_3$ is the unit cell volume

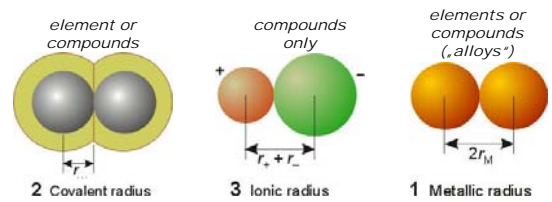
Properties of the reciprocal lattice

- Note $\mathbf{a}_i \cdot \mathbf{b}_j = \delta_{ij}$
- So $\mathbf{a}_1 \cdot \mathbf{b}_1 = 1$, but $\mathbf{a}_1 \cdot \mathbf{b}_2 = 0$ and $\mathbf{a}_1 \cdot \mathbf{b}_3 = 0$ etc.
 - This is the origin of the term reciprocal lattice.
 - The reciprocal lattice and real space lattice are orthonormal
- Any point on the reciprocal lattice can be specified by a vector $\mathbf{H}_{hkl} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$ (hkl are integers)
 - This vector is perpendicular to the plane in real space with Miller indices (hkl)
 - The length of this vector $H_{hkl} = 1/d_{hkl}$ where d_{hkl} is the interplanar spacing in real space
 - We get to represent a whole family of planes in real space by a single point in reciprocal space

Geometrical relationship between real and reciprocal space



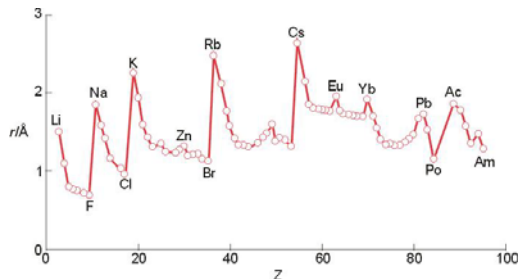
Different types of atomic radii (atoms can be treated [badly] as hard spheres)



Metals Atomic radius = $d/2$ in element (a.k.a. metallic radius)
Covalent radius = $d/2$ in single bond

Non-metals Atomic radius = $d/2$ in element
Covalent radius = $d/2$ in single bond

Variation of atomic radii through the Periodic table



Other quantities that show a systematic variation through the Periodic System: Electronegativity, Ionization Potential ...

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

- Crystalline materials can be **single crystals** or **polycrystalline**. Material properties generally vary with single crystal orientation (i.e., they are **anisotropic**). But, in polycrystals with randomly oriented grains, properties are generally non-directional (i.e., they are **isotropic**).
- 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.