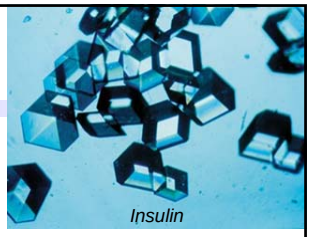
Sapphire: cryst. Al_2O_3



Insulin

Chapter 3: The Structure of Crystalline Solids

Crystal:

a solid composed of atoms, ions, or molecules arranged in a pattern that is repeated in three dimensions

A material in which atoms are situated in a repeating or periodic array over large atomic distances

3.1 Classification

- Crystalline materials

- atoms(ions or molecules) in repeating 3D pattern (called a lattice)
- long-range order; ex.: NaCl,

- Amorphous (noncrystalline) materials

- Short range order, not periodic; ex.: liquid water, glass

- Fractals

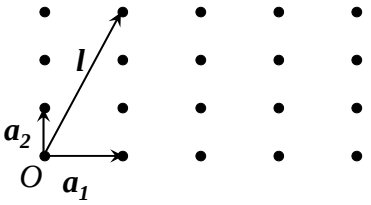
- Long-range order, symmetry, but not repeating

- Liquid crystals

- long range order of one type; disorder of another
- Nematic and smectic

Translational Symmetry

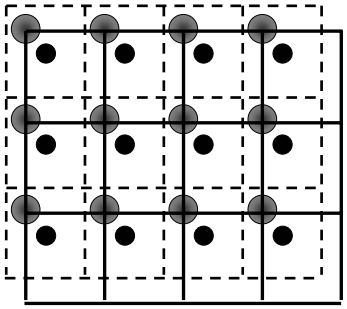
Consider perfect ideal solid



The translational group represented by **space lattice or Bravais net**

Lattice sites defined by:

$$l = l_1 a_1 + l_2 a_2 + l_3 a_3$$

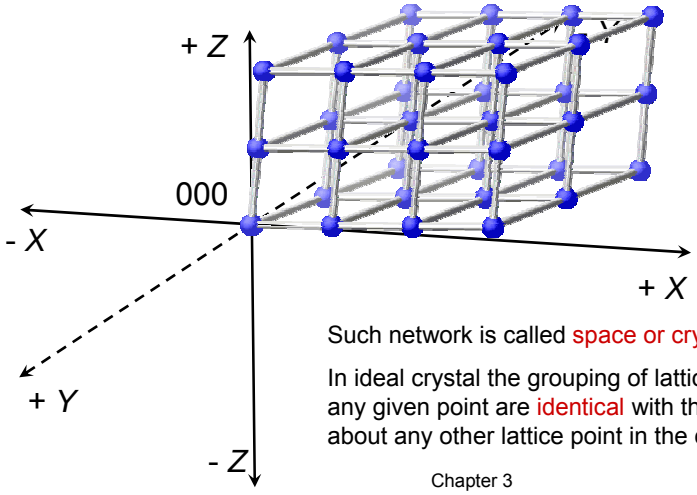


The actual definition of a unit cell is to some extent arbitrary

NB: atoms do not necessarily coincide with space lattice

Space lattice

Positions of atoms in crystals can be defined by referring the atoms to the point of intersection with 3D coordinate system

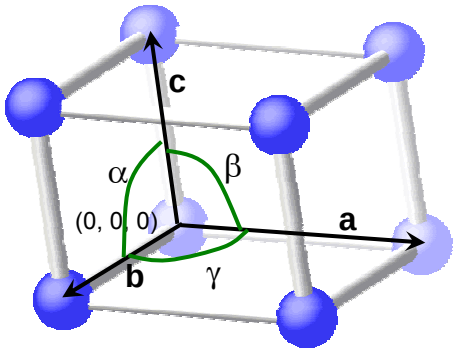


Such network is called space or crystal lattice

In ideal crystal the grouping of lattice points about any given point are identical with the grouping about any other lattice point in the crystal lattice

Unit cell

$\mathbf{a} = \vec{a}$



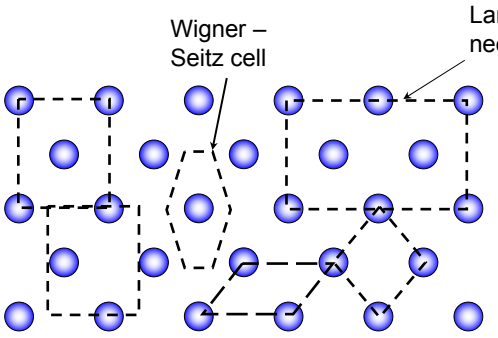
The size and shape of the unit cell can be described by three lattice vectors: **a, b, c**

or the axial lengths *a, b,* and *c* and interaxial angles α, β, γ

NB!!!: atoms do not necessarily coincide with lattice points

How to choose unit cell?

Unit cell: a convenient repeating unit of a crystal lattice; the axial lengths and axial angles are the lattice constants of the unit cell



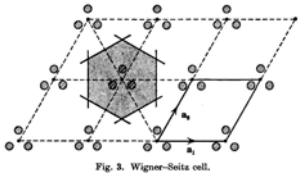


Fig. 3. Wigner–Seitz cell.

Wigner – Seitz Cell : place the symmetry centre in the centre of the cell; draw the perpendicular bisector planes of the translation vectors from the chosen centre to the nearest equivalent lattice site

Crystal systems (7)

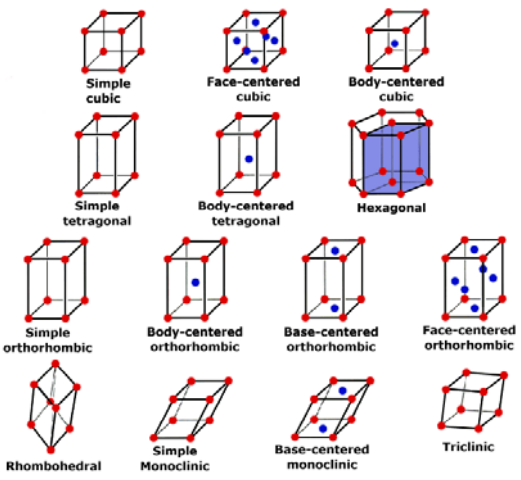
symmetry

Classification of space lattices by crystal system

Crystal system	Axial lengths and interaxial angles	Space lattice
Cubic	Three equal axes at right angles $a = b = c, \alpha = \beta = \gamma = 90°$	Simple cubic Body-centered cubic Face-centered cubic
Tetragonal	Three axes at right angles, two equal $a = b \neq c, \alpha = \beta = \gamma = 90°$	Simple tetragonal Body-centered tetragonal
Orthorhombic	Three unequal axes at right angles $a \neq b \neq c, \alpha = \beta = \gamma = 90°$	Simple orthorhombic Body-centered orthorhombic Base-centered orthorhombic Face-centered orthorhombic
Rhombohedral	Three equal axes, equally inclined $a = b = c, \alpha = \beta = \gamma \neq 90°$	Simple rhombohedral
Hexagonal	Two equal axes at 120°, third axis at right angles $a = b \neq c, \alpha = \beta = 90°, \gamma = 120°$	Simple hexagonal
Monoclinic	Three unequal axes, one pair not at right angles $a \neq b \neq c, \alpha = \gamma = 90° \neq \beta$	Simple monoclinic Base-centered monoclinic
Triclinic	Three unequal axes, unequally inclined and none at right angles $a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90°$	Simple triclinic

crystallographic point group – set of symmetry operations, (ex.: rotations or reflections), that leave a point fixed while moving each atom of the crystal to the position of an atom of the same kind

14 Bravais Lattices



230 lattices or spacegroups

Lowest in symmetry #1:

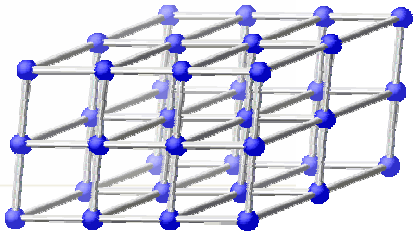
Short International symbol: $P\,1$

Schönflies symbol: C_1^1 Triclinic

Spacegroup number: No. 1

Full International symbol: $P\,1$

Multiplicity: 1



$a \neq b \neq c$; $\alpha \neq \beta \neq \gamma \neq 90^o$

Even higher symmetry structure

Short International symbol: $F\,d\,\bar{3}\,m$

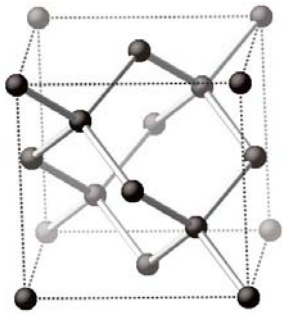
Schönflies symbol: O_h^7 Cubic

Spacegroup number: No. 227

Full International symbol: $F\,4_1/d\,\bar{3}\,2/m$

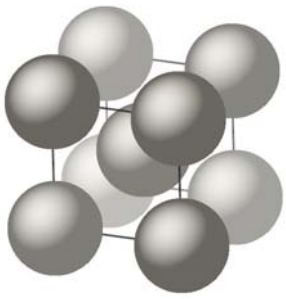
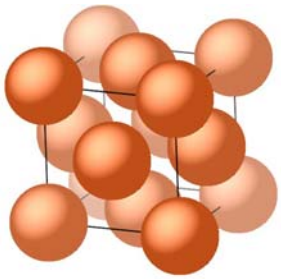
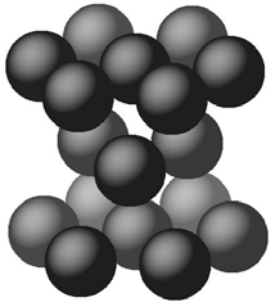
ORIGIN CHOICE 1: origin at $-\frac{1}{8}, -\frac{1}{8}, -\frac{1}{8}$ from centre of

Multiplicity: 192

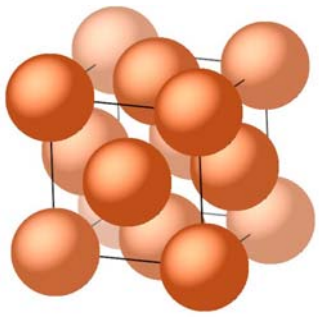


Metallic crystal structures (will talk about metal oxides later)

- >90% of elemental metals crystallize upon solidification into **3** densely packed crystal structures:

Body-centered cubic (bcc)	Face-centered cubic (fcc)	Hexagonal close-packed (hcp)
		
ex.: Fe, W, Cr	ex.: Cu, Ag, Au	ex.: Zr, Ti, Zn

Important to know:



- Distance between atoms (d)
  - in terms of *a*
- Number of atoms in the unit cell
  - each corner atoms shared by 8 cells: 1/8
  - each face atom shared by 2 cells: ½
  - each edge atom shared by 4 cells: 1/4
- Coordination number
  - Number of nearest neighbours (n.n.); for metals all equivalent
- Atomic Packing Factor (APF)

  APF = Volume of atoms in unit cell / Volume of unit cell (a^3)

Coordination number

The number of atoms that surround a central atom in a solid is called **coordination number**

C.N. = 3 Corners of triangle 	C.N. = 4 Corners of tetrahedron 
C.N. = 6 Corners of octahedron 	C.N. = 8 Corners of cube 

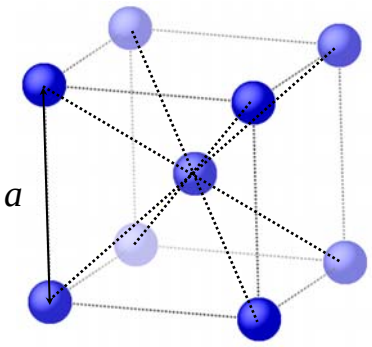
Body-Centered Cubic (bcc)

Distance between atoms:

Atoms/cell:

Coordination number:

Atomic Packing Factor (APF):



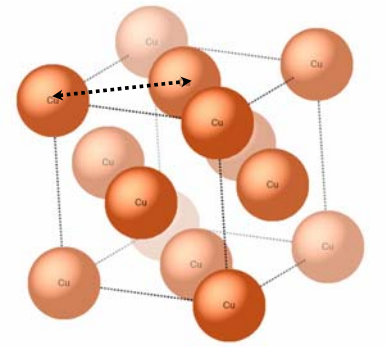
Face-Centered Cubic (fcc)

Distance between atoms:

Atoms/cell:

Coordination number:

Atomic Packing Factor (APF):



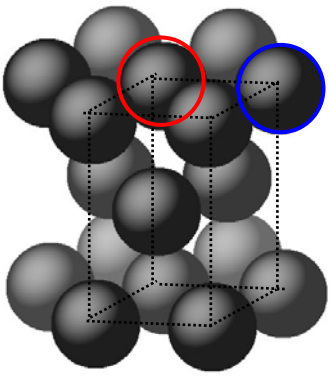
Hexagonal close-packed (hcp)

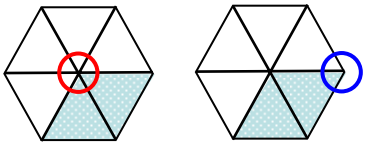
Distance between atoms: *a and c*

Atoms/cell:

Coordination number:

Atomic Packing Factor (APF):

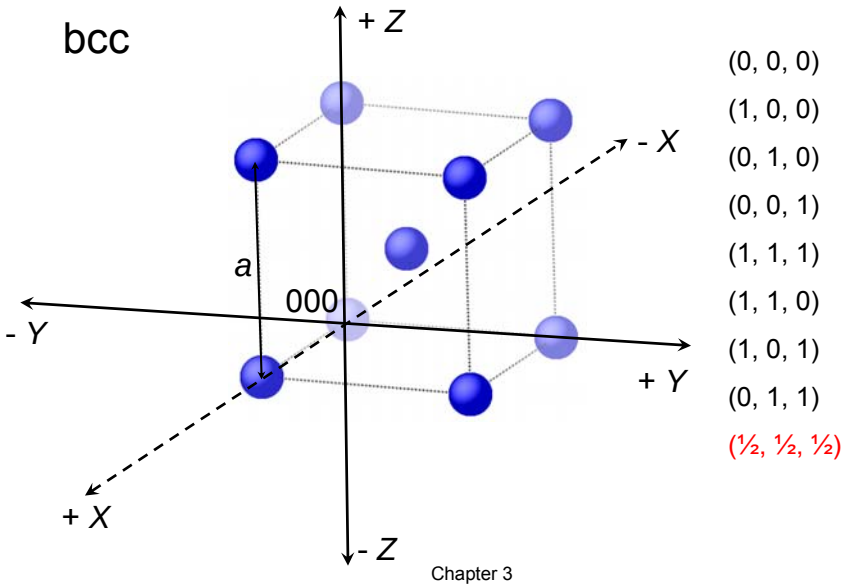




Density calculations

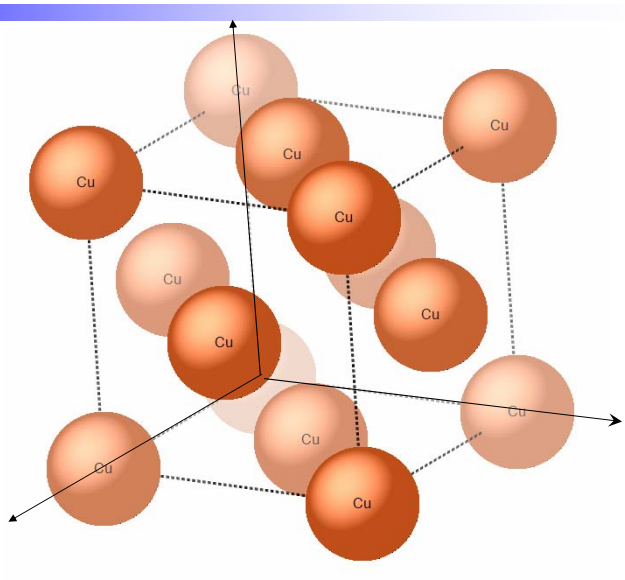
- Calculate theoretical density of gold (Au), if the molar density is given: w = 0.1970 kg/mol; and *a*(Au)=0.408nm

3.4 Atom coordinates in the cubic unit cell

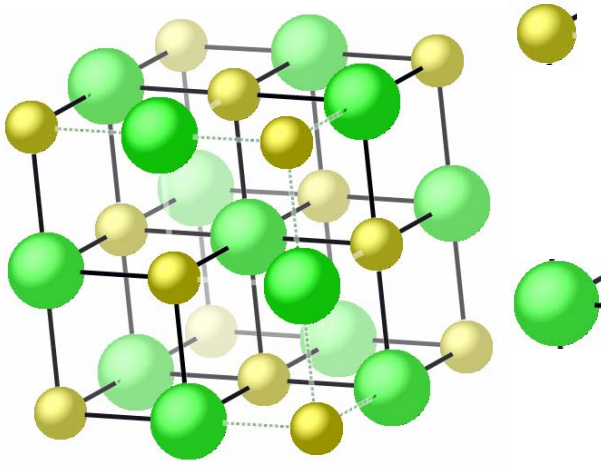


Face-Centered Cubic (fcc)

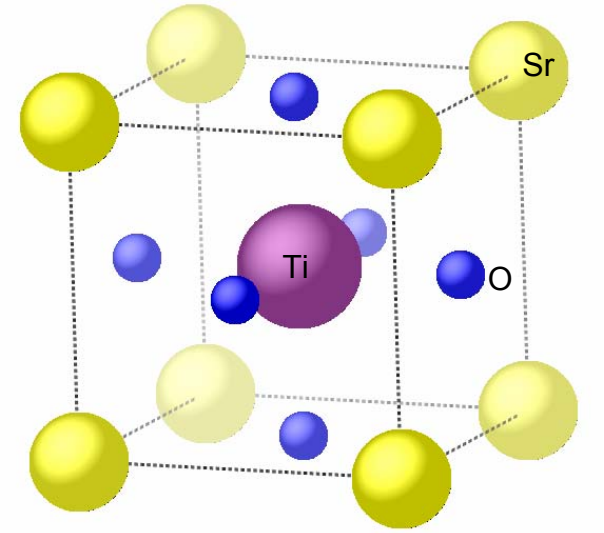
8 Cu	6 Cu
(0, 0, 0)	(½, ½, 0)
(1, 0, 0)	(0, ½, ½)
(0, 1, 0)	(½, 0, ½)
(0, 0, 1)	(½, ½, 1)
(1, 1, 1)	(1, ½, ½)
(1, 1, 0)	(½, 0, ½)
(1, 0, 1)	
(0, 1, 1)	



Sodium Chloride (NaCl)

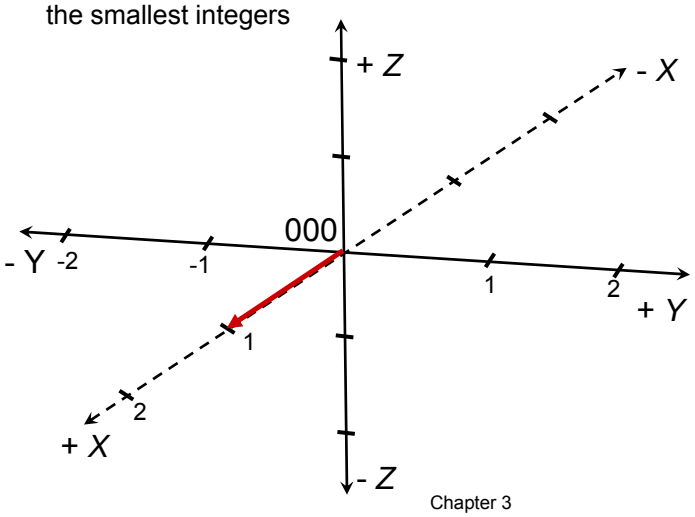


Strontium titanate ($Sr_xTi_yO_z$)



3.5 Directions in cubic unit cell

The crystallographic direction indices [u, v, w] - the vectors of the direction resolved along each of the coordinate axes and reduced to the smallest integers

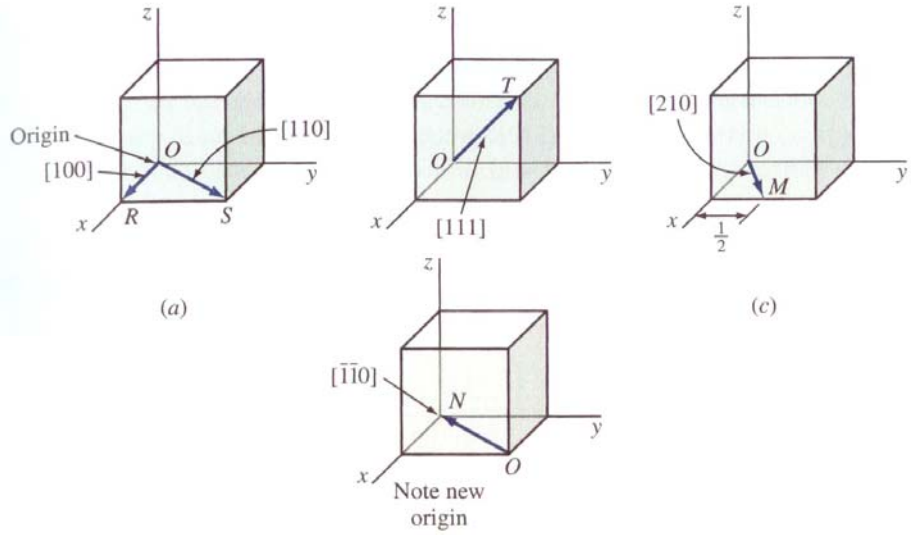


[2, 0, 0]

=

[1, 0, 0]

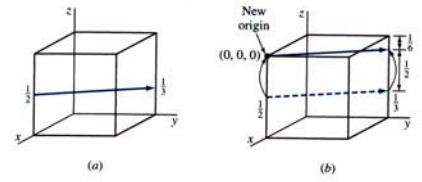
Examples:



Crystallographically equivalent

- Parallel direction vectors have the same direction indices:

ex.: determine the direction indices of the cubic direction shown



- Directions are crystallographically equivalent if the atom spacing along each directions are the same

ex.: [100], [010], [001], [-100], [0-10], [00-1] = <100>

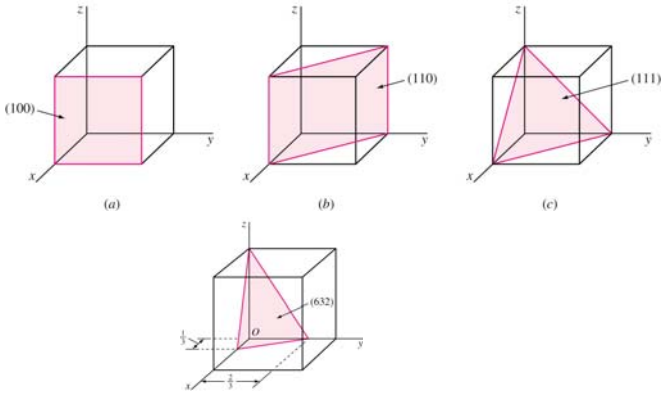
3.6 Miller indices for crystallographic planes in cubic unit cells

- Miller indices of a crystal plane are the reciprocals of the fractional intercepts that the plane makes with the crystallographic x, y, and z axes

  Most important crystallographic planes: (100), (110), (111)

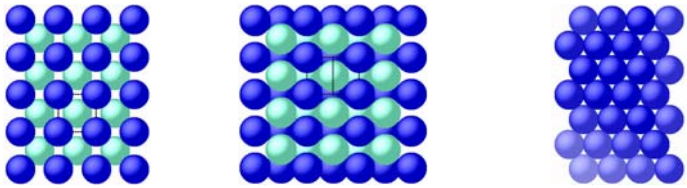
(100) intercepts:

1, ∞, ∞

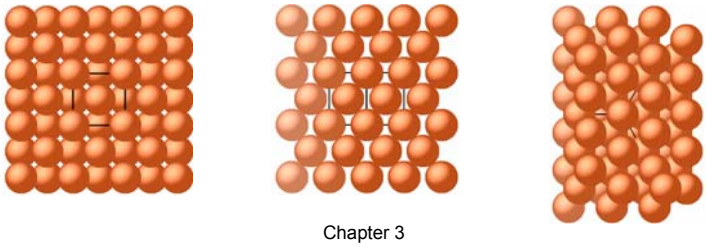


Atomic Packing in Different Planes

- *bcc* (100) (110) (111)

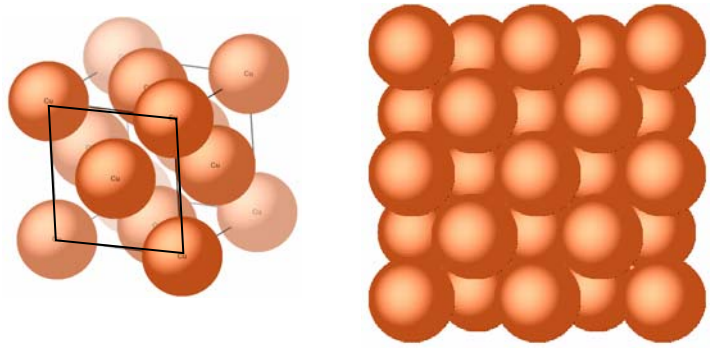


- *fcc* (100) (110) (111)



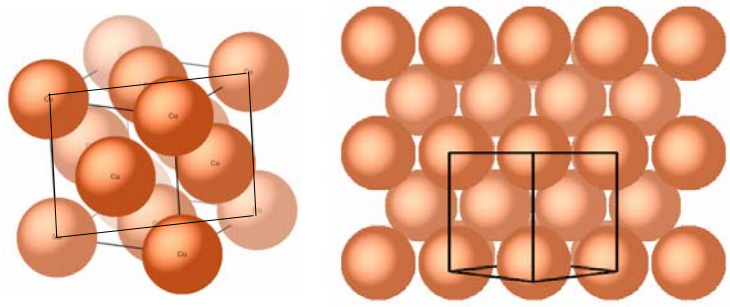
fcc crystallographic planes

Cu (100)



fcc crystallographic planes

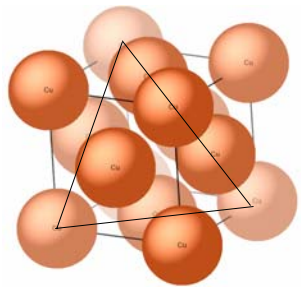
Cu (110)

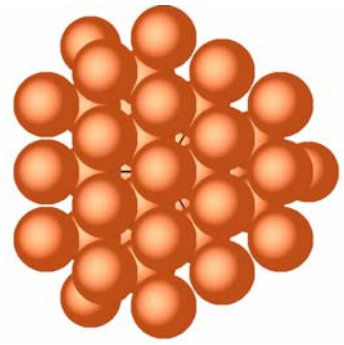


Anisotropy of properties in two directions

fcc crystallographic planes

Cu (111)

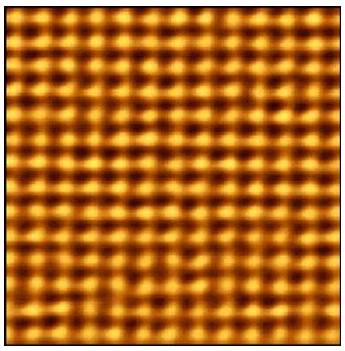




3 fold symmetry

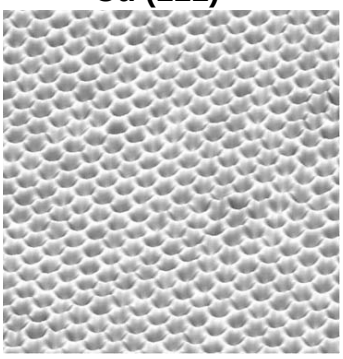
STM (Scanning tunneling microscopy)

Cu (100)



Atomically resolved STM of Cu(100)

Cu (111)



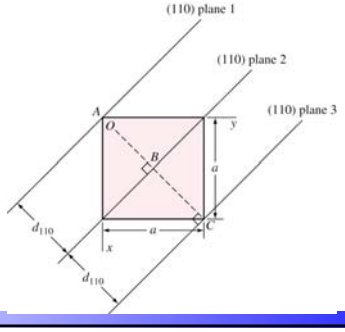
Custom Low Temperature UHV STM image of atomic resolution pattern on Cu(111). Image taken at 4.2K.

Crystallographic planes

- Single plane $(h\ k\ l)$
- Notation: planes of a family $\{h\ k\ l\}$

  $(100); (010); (001); \ldots \Rightarrow \{100\}$
- *Only for cubic systems*: the direction indices of a direction perpendicular to a crystal plane have the same Miller indices as a plane
- Interplanar spacing d_{hkl}:

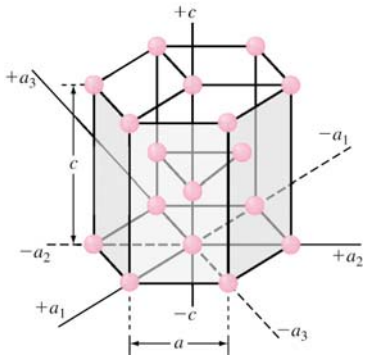
$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$



3.7 Planes in hexagonal crystals

4 coordinate axes (a_1, a_2, a_3, and c) of the HCP structure (instead of 3)

Miller-Bravais indices - ($h\ k\ i\ l$) – based on 4 axes coordinate system



a_1, a_2, and a_3 are 120° apart: $h\ k\ i$

c axis is 90°: l

3 indices (rarely used):

$h + k = -l$

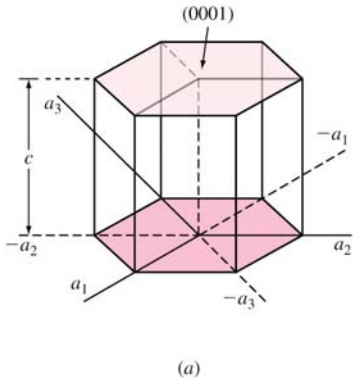
$(h\ k\ i\ l) \Rightarrow (h\ k\ l)$

Basal and Prizm Planes

Basal planes;

$a_1 = \infty$; $a_2 = \infty$; $a_3 = \infty$; $c = 1$

$\Rightarrow$ (0 0 0 1)

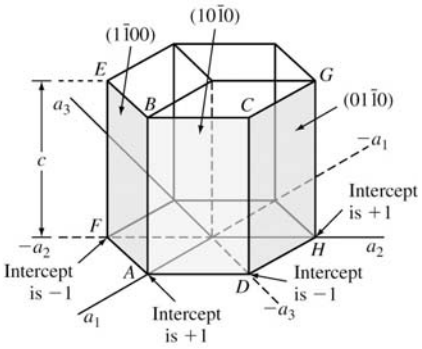


(a)

Prizm planes: ABCD

$a_1 = +1$; $a_2 = \infty$; $a_3 = -1$; $c = \infty$

$\Rightarrow$ (1 0 -1 0)

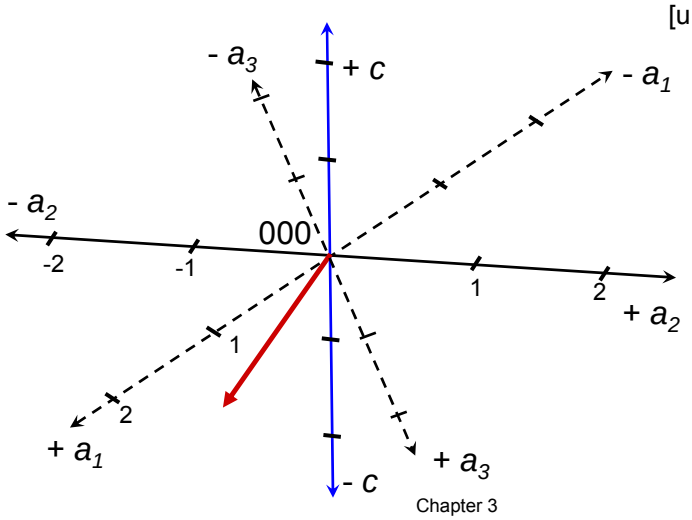


(b)

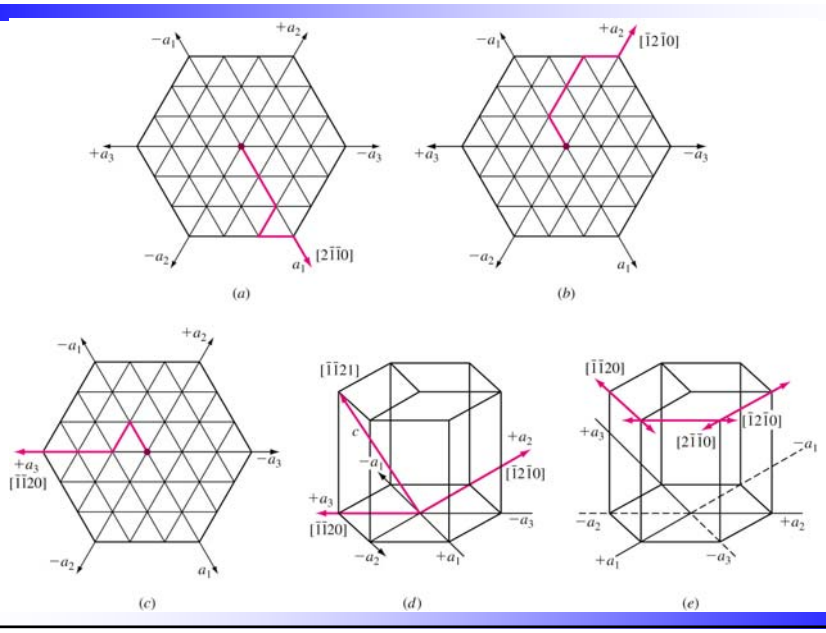
Directions in hexagonal crystals

[u, v, t, w] or

[u, v, w] u + v = -t

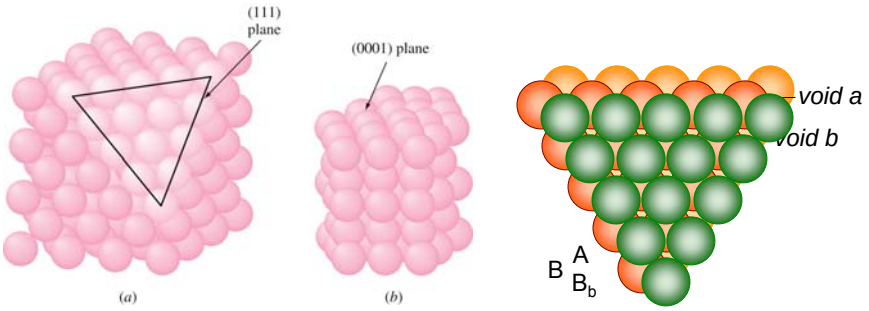


Principle directions in hcp



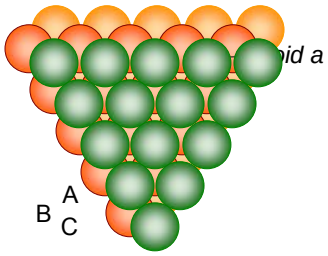
3.8 Comparison of crystal structures

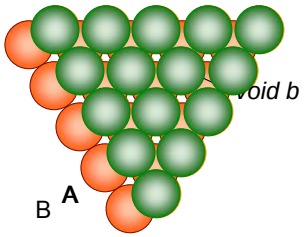
FCC and HCP metal crystal structures



- (111) planes of fcc have the same arrangement as (0001) plane of hcp crystal
- 3D structures are not identical: stacking has to be considered

FCC and HCP crystal structures





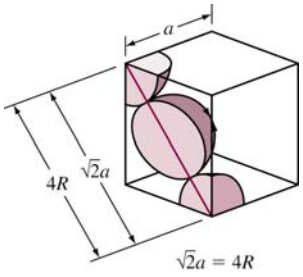
fcc	hcp
B plane placed in *a* voids of plane A	B plane placed in a voids of plane A
Next plane placed in *a* voids of plane B, making a new C plane	Next plane placed in *a* voids of plane B, making a new A plane
Stacking: ABCABC…	Stacking: ABAB…

3.9 Volume, planar, and linear density unit cell calculations

Volume density of a metal can be obtained by using the hard-sphere atomic model for the crystal structure unit cell

$$Volume\_density\_of\_metal = \rho_v = \frac{mass/unit\_cell}{volume/unit\_cell}$$

Q.: Copper has an *fcc* crystal structure and an atomic radius of 0.1278nm. Assuming the Cu atoms to be hard spheres that touch each other along the face diagonal of the fcc unit cell, calculate a theoretical value for the density of Cu in kg/m^3.



3.10 Allotropy and polymorphism (=..?)

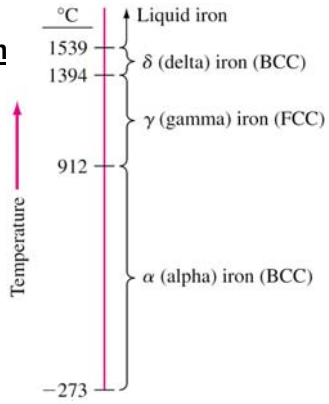
Allotropy – the ability of element to exist in two or more crystalline structures

Fe: bcc ⇒ fcc ⇒ bcc

In case of compound it is called **polymorphism**

Carbon allotropic forms: ?

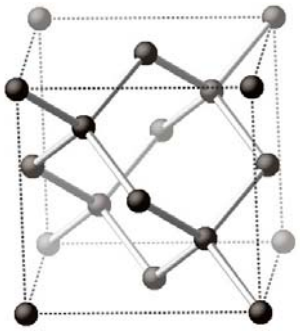
1. diamond
2. graphite
3. fullerene or buckyballs
4. nanotubes or buckysheets



Carbon and its allotropes

Diamond

- Cubic structure
  (0, 0, 0) (1/2, 1/2, 0) (1/4, 1/4, 1/4)
- Covalently bonded sp^3 orbitals
- Isotropic
- Stiffest, hardest (?) and least compressible
- High thermal conductivity
- But… no electrical conductivity



Graphite

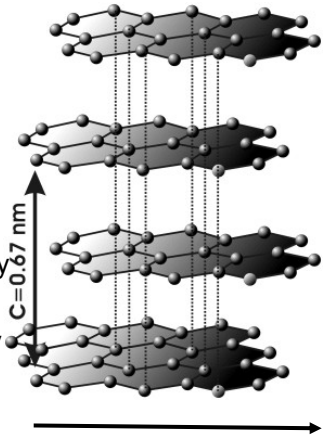
Graphite

- hexagonal structure
- covalently bonded sp^2 orbitals and weak secondary bonds between planes
- anisotropic
- High thermal and electrical conductivity

(in plane)

- Bad thermal and electrical conductivity

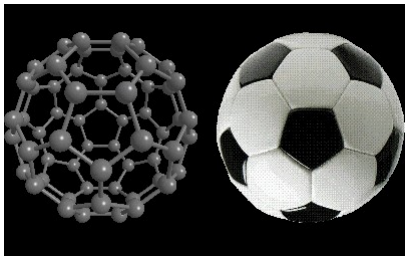
(between plane, along c axis)



Fullerenes (Buckyballs)

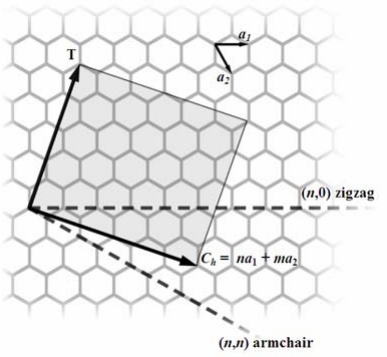
Discovered in 1985 by Harry Kroto and Richard Smalley while blasting graphite with a laser (C_{30} to C_{100})

- 12 pentagons and 20 hexagons
- crystallize in fcc structure
- isotropic
- bonding: covalent and van der Waals forces

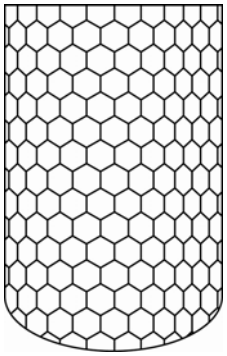


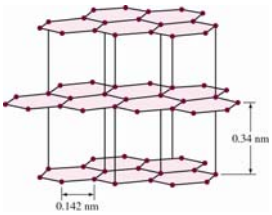
Carbon nanotubes

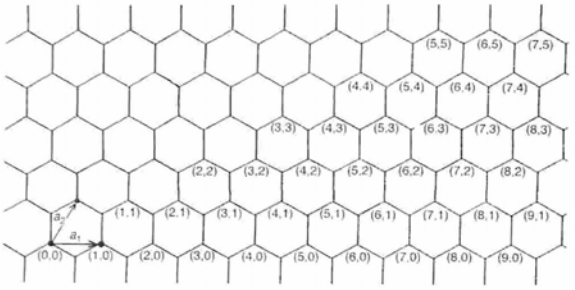
- hexagonal
- properties depend on the structure
- more later…



Carbon Nanotubes







The structure can be specified by vector **(n, m)** which defines how the graphene sheet is rolled up

A nanotube with the indices (6,3): the sheet is rolled up so that the atom (0,0) is superimposed on the one labeled (6,3)

m = 0 for all zig-zag tubes, while n = m for all armchair tubes

Summary

- Unit cells, crystal systems and lattices
- Atomic coordinates and number of atoms in the unit cell
- Crystallographic directions and crystal planes
- Coordination numbers

- Finding distances between atoms and planes, and characteristic angles
- In order to find all this parameters: X-ray diffraction, electron microscopy (later)

Problems

3.1. Molybdenum is bcc and has an atomic radius of 0.14nm. Calculate a value for its lattice constant a in nanometers.

3.2. Figure below illustrates unit cell of diamond crystal structure.
(a) How many carbon atoms are there per unit cell?
(b) What is the coordination number for each carbon atoms? (C.N is the number of equidistant nearest neighbors to an atom in a crystal structure)

3.3. Draw direction vectors in unit cubes for the following directions: (a) [111], (b) [1-1-1], (c) [-12-1]; (d) [-1-13]

3.4. Define the Miller indices of the cubic crystal plane that intersects the following position coordinates: (a)1/2, 0, 1/2); (0, 0, 1); (1, 1, 1); (b) (0, 0, 1/2); (1, 0, 0); (1/2, 1/4, 0)

3.5. Draw in unit cubes the crystal planes that have the following Miller indices:
(a) (1-1-1); (b) (10-2), (c) (1-21), (d) (21-3)

3.6 Allotropic phase change. Iron is observed to undergo a transformation from bcc to fcc cubic structure at 921^{0}C. Assuming that in each case the atoms behave as hard spheres and that the size of these spheres is not affected by the transformation, determine the percentage change in volume that occurs.