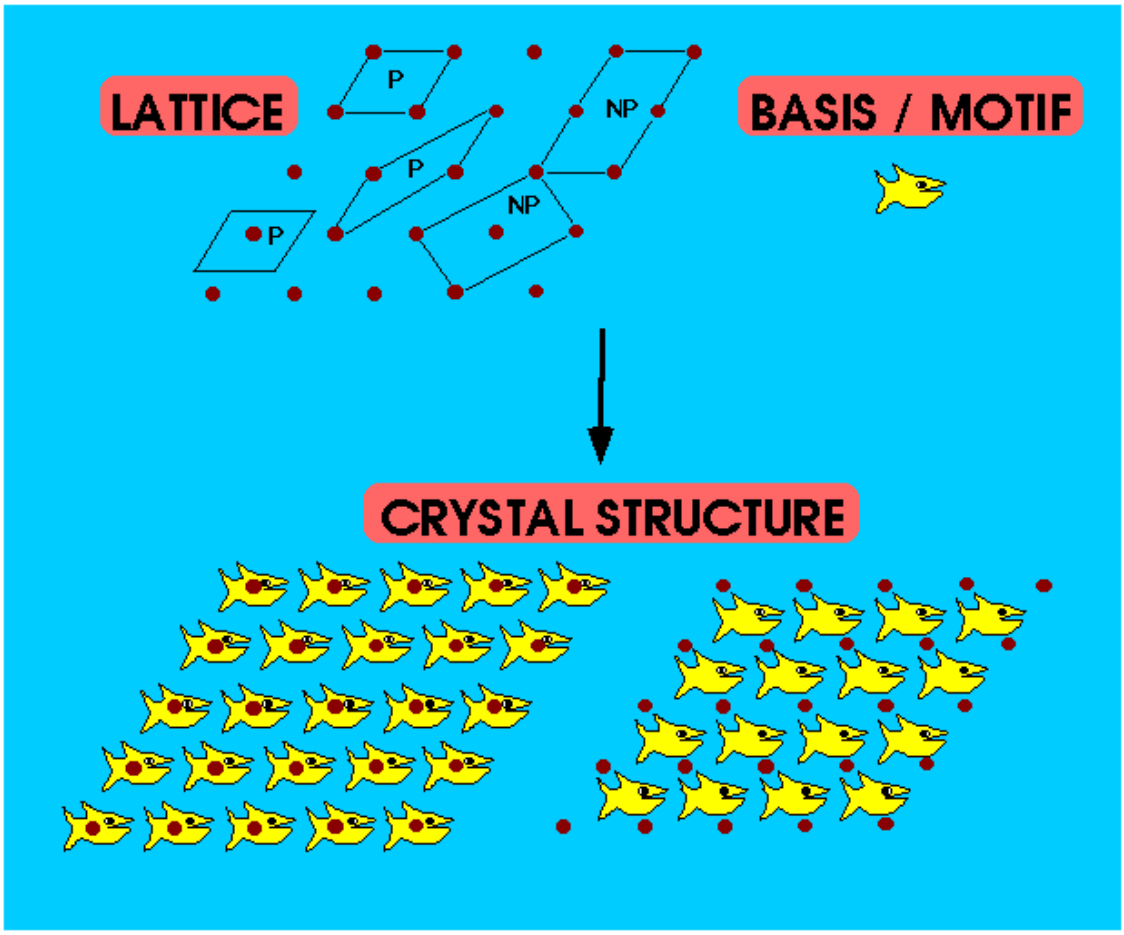


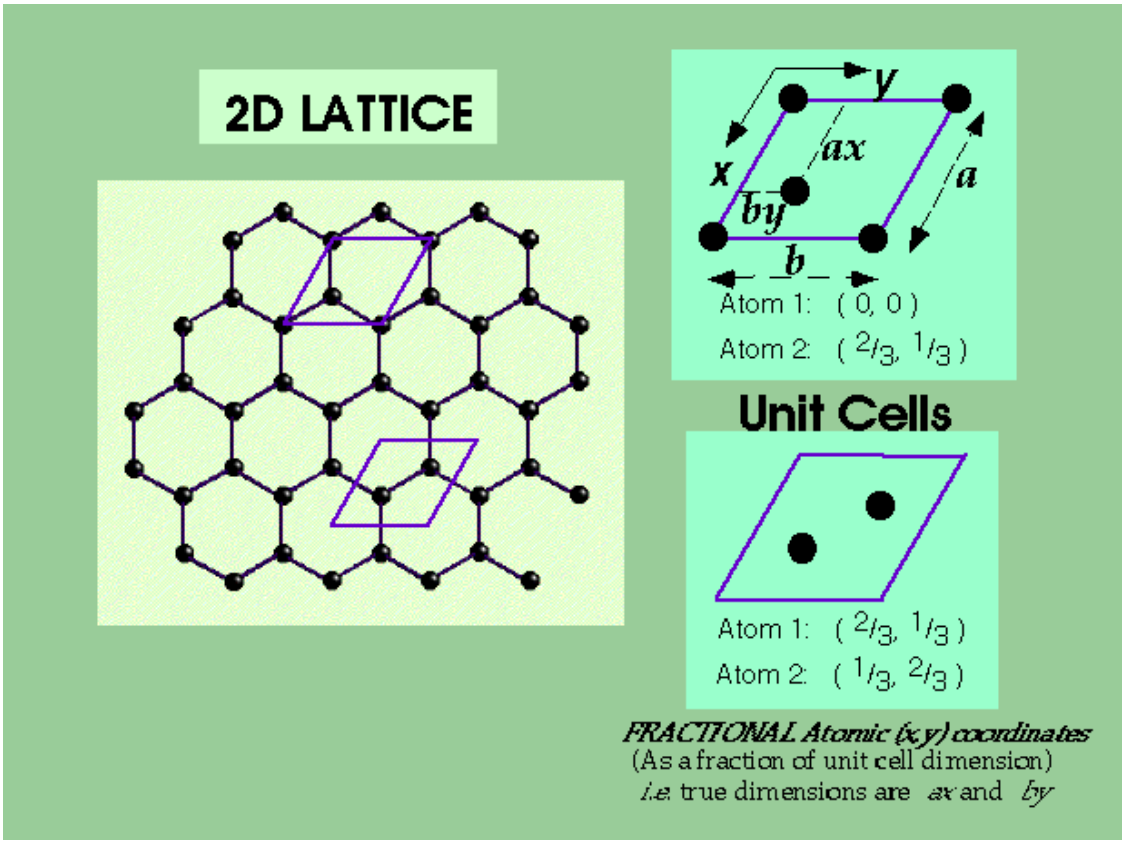
- Don’t mix up atoms with lattice points
- Lattice points are infinitesimal points in space
- Atoms are physical objects
- Lattice Points do not necessarily lie at the centre of atoms

UNIT CELL = The smallest component of the crystal, which when stacked together with pure translational repetition reproduces the whole crystal

- **Primitive** (**P**)unit cells contain only a ***single lattice point***

2D LATTICES

e.g. the fused hexagonal pattern of a **single layer of GRAPHITE**



Counting Lattice Points/Atoms in 2D Lattices

- Unit cell is **Primitive (1 lattice point)** but contains **TWO atoms** in the Motif
- Atoms at the **corner** of the 2D unit cell contribute only $^{1}/_{4}$ to unit cell count
- Atoms at the **edge** of the 2D unit cell contribute only $^{1}/_{2}$ to unit cell count
- Atoms **within** the 2D unit cell contribute **1** (*i.e.* uniquely) to that unit cell

2-Dimensional Lattice Symmetries were famously exploited by the artist Escher in many patterns

- A tutorial on the 2D tessellations of Escher
- A really fun way to create your own 2D patterns with different lattice symmetries is the "Escher Web Sketch" Java program of Wes Hardaker and Gervais Chapuis

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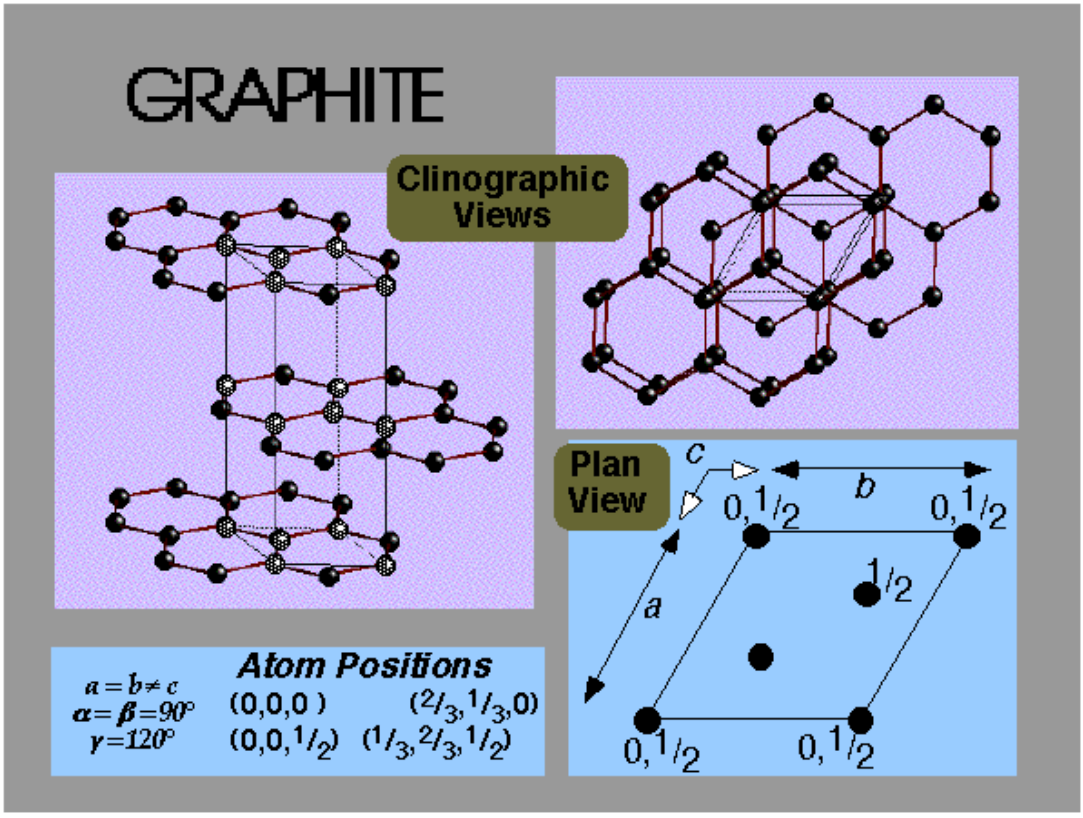
Analysing a 3D solid

e.g. **Graphite** = a staggered arrangement of stacked hexagonal layers

Perspective: Clinographic views of solids

Projection onto a Plane: Plan views of solids

GRAPHITE



Unit Cell Dimensions

* ***a***, ***b*** and ***c*** are the unit cell edge lengths

* **a**, **b** and **g** are the angles (a between *b* and *c*, etc....)

Counting Atoms in 3D Cells

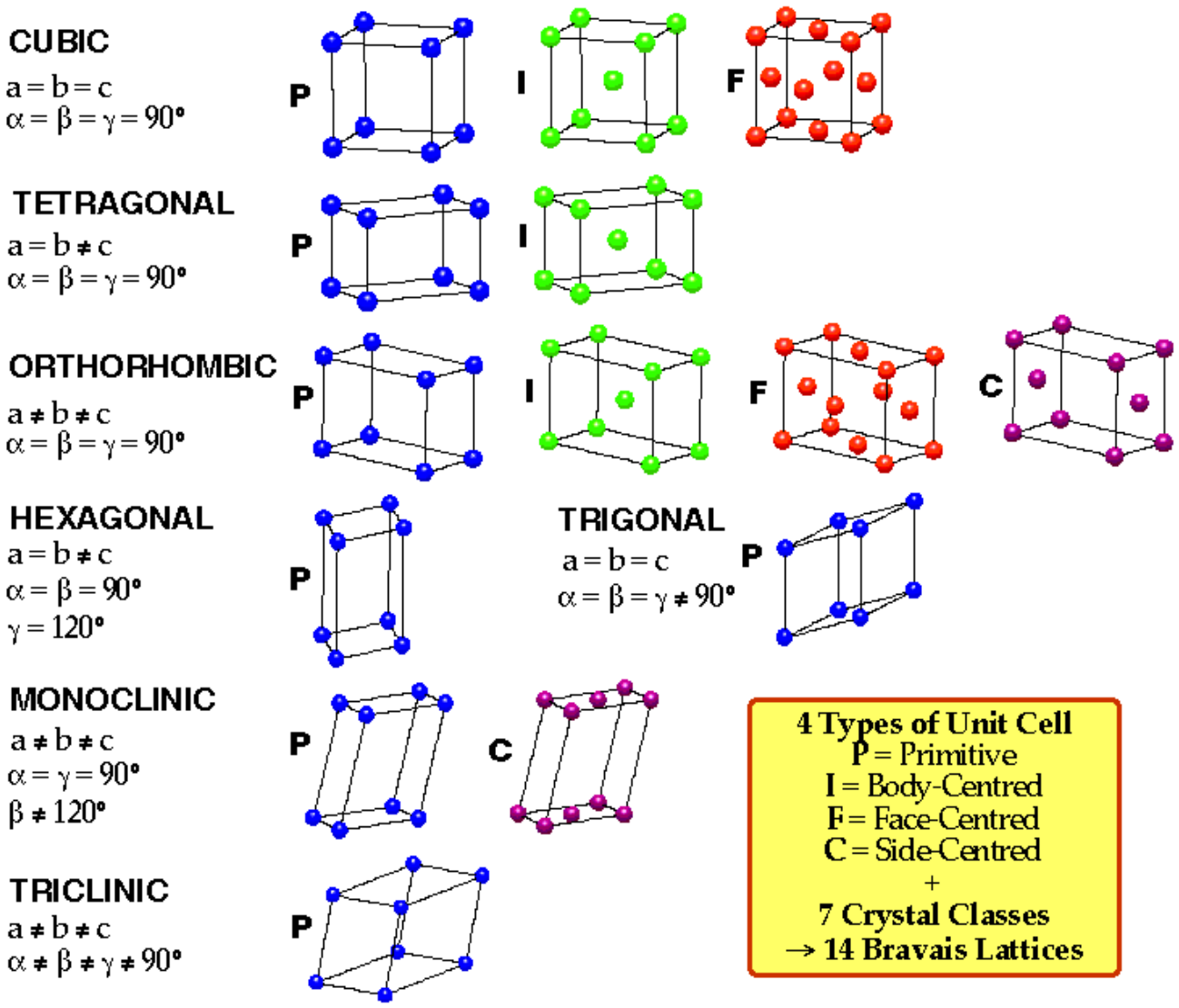
Atoms in different positions in a cell are shared by differing numbers of unit cells

- Vertex atom shared by **8** cells Þ $\mathbf{^1/_8}$ atom per cell
- Edge atom shared by **4** cells Þ $\mathbf{^1/_4}$ atom per cell
- Face atom shared by **2** cells Þ $\mathbf{^1/_2}$ atom per cell
- Body unique to **1** cell Þ **1** atom per cell

On combining 7 Crystal Classes with 4 possible unit cell types Symmetry indicates that only 14 3-D lattice types occur

The 14 possible **BRAVAIS LATTICES**

{note that spheres in this picture represent lattice points, not atoms!}



Examine the 14 Bravais Lattices in Detail

Cubic-P, Cubic-I, Cubic-F, Tetragonal-P, Tetragonal-I, Orthorhombic-P, Orthorhombic-I, Orthorhombic-F, Orthorhombic-C, Hexagonal-P, Trigonal-P, Monoclinic-P, Monoclinic-C, Triclinic-P

If you have the Chemscape Chime Plug-in you can manipulate the 14 Bravais lattices at the University of Texas, Austin

Combining these 14 Bravais lattices with all possible symmetry elements

→ **230** different **Space Groups**

For applications of different geometry lattice theories to simple structures see:-

- Russell Chu's views of solids as interpenetrating ccp and hcp lattices, including stereoview pictures.
- Scott Childs's application of Synergetic Geometry to crystal structure description

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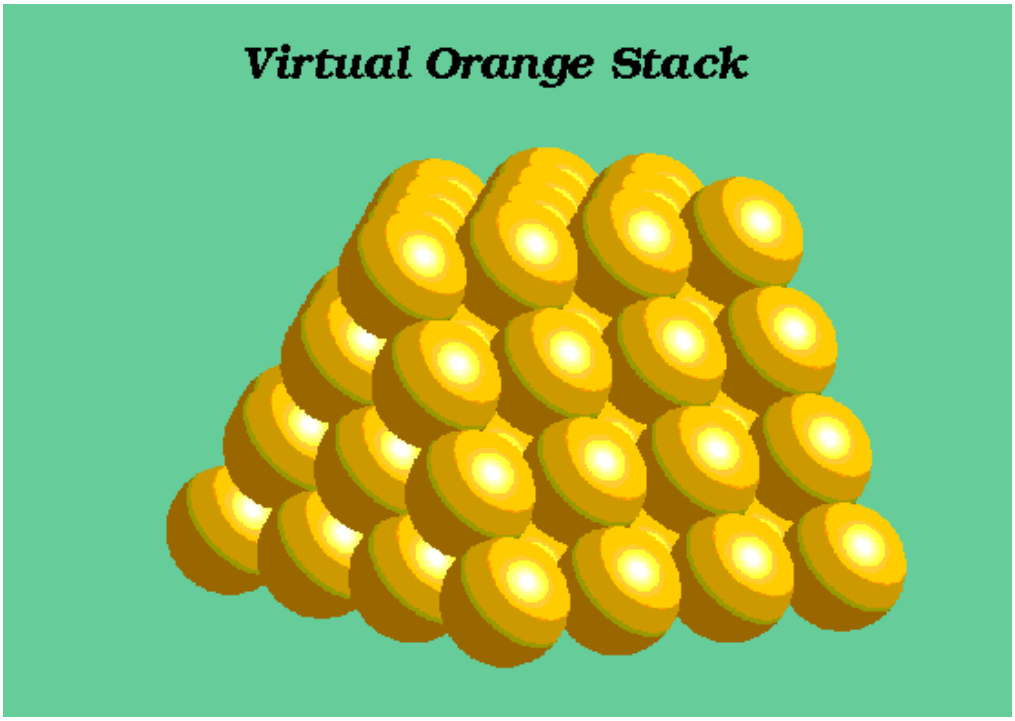
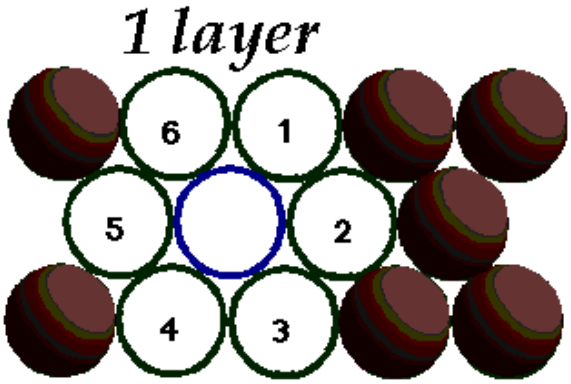
1926 Goldschmidt proposed atoms could be considered as packing in solids as **hard spheres**

This reduces the problem of examining the packing of like atoms to that of examining the most efficient packing of any spherical object - *e.g.* have you noticed how oranges are most effectively packed in displays at your local shop?



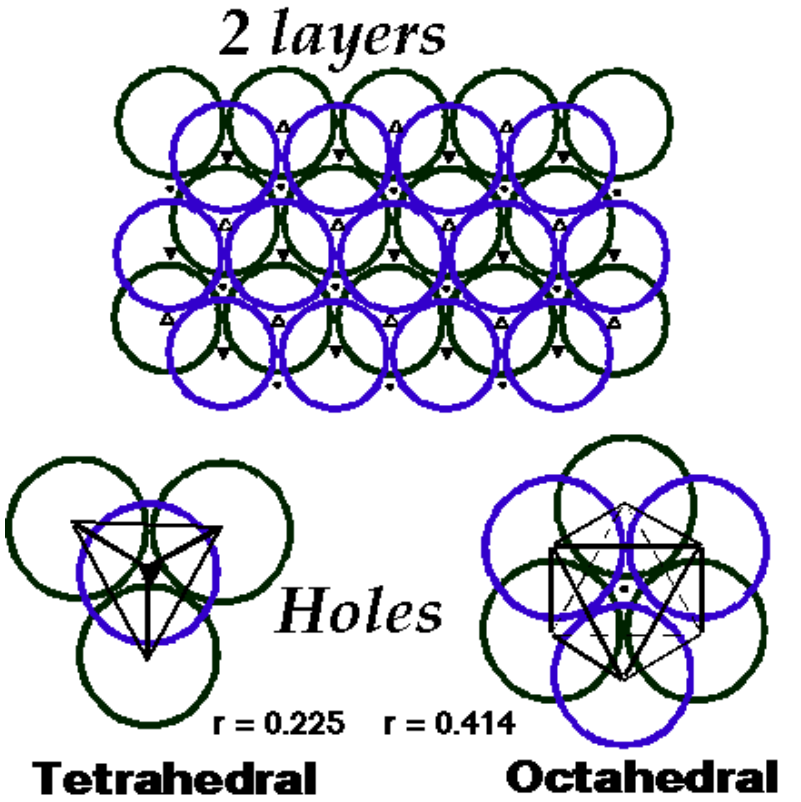
CLOSE-PACKING OF SPHERES

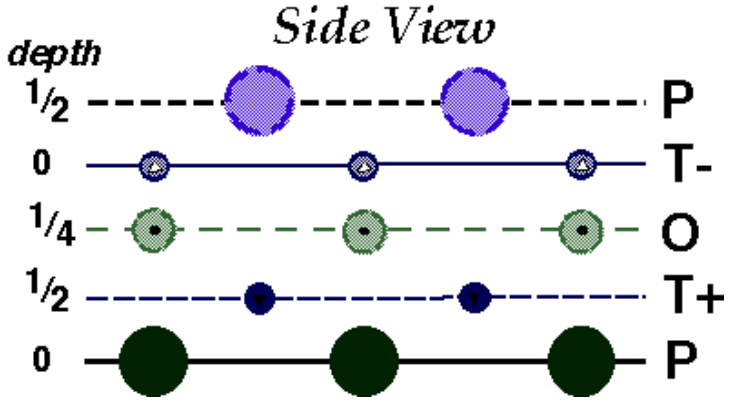
A *single layer* of spheres is closest-packed with a **HEXAGONAL** coordination of each sphere



A *second layer* of spheres is placed in the **indentations** left by the first layer

- **space** is trapped between the layers that is not filled by the spheres
- **TWO** different types of **HOLES** (so-called ***INTERSTITIAL*** sites) are left
  - **OCTAHEDRAL** (**O**) holes with **6** nearest sphere neighbours
  - **TETRAHEDRAL** (**T±**) holes with **4** nearest sphere neighbours



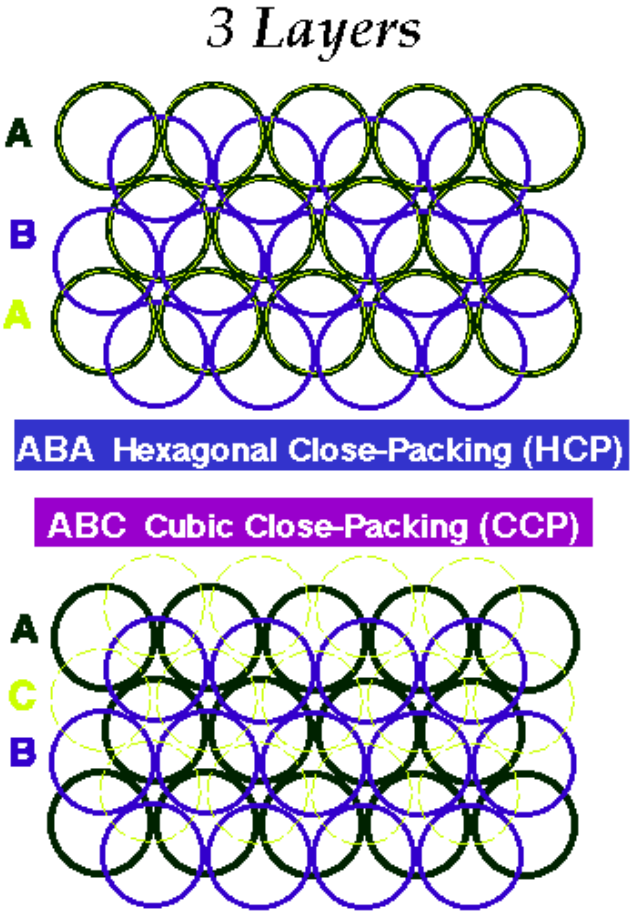


{P = sphere, O = octahedral hole, T+ / T- = tetrahedral holes)

When a *third layer* of spheres is placed in the indentations of the second layer there are TWO choices

- The third layer lies in indentations directly in line (***eclipsed***) with

the 1st layer
    - Layer ordering may be described as ABA
- The third layer lies in the alternative indentations leaving it ***staggered*** with respect to both previous layers
    - Layer ordering may be described as ABC



Close-Packed Structures

The most efficient way to fill space with spheres

Is there another way of packing spheres that is more space-efficient?

In 1611 Johannes Kepler asserted that there was no way of packing equivalent spheres at a greater density than that of a face-centred cubic arrangement. This is now known as the **Kepler Conjecture**.

This assertion has long remained without rigorous proof, but in August 1998 Prof. Thomas Hales of the University of Michigan announced a computer-based solution. This proof is contained in over 250 manuscript pages and relies on over 3 gigabytes of computer files and so it will be some time before it has been checked rigorously by the scientific community to ensure that the Kepler Conjecture is indeed proven!

- An article by Dr. Simon Singh © Daily Telegraph, 13th August 1998

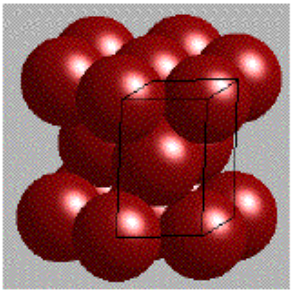
Features of Close-Packing

- Coordination Number = **12**
- **74%** of space is occupied
- Largest interstitial sites are:-
  - octahedral (O) (r = 0.414) ~1 per sphere
  - tetrahedral (T±) (r = 0.225) ~2 per sphere

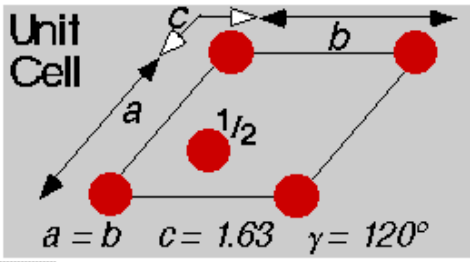
Simplest Close-Packing Structures

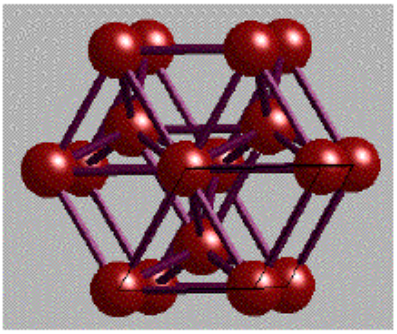
- ABABAB.... repeat gives Hexagonal Close-Packing (**HCP**)
  - Unit cell showing the full symmetry of the arrangement is *Hexagonal*
    - Hexagonal: $a = b$, $c = 1.63a$, a = b = 90°, g = 120°
    - 2 atoms in the unit cell: (0, 0, 0) ($^2/_3$, $^1/_3$, $^1/_2$)
- ABCABC.... repeat gives Cubic Close-Packing (**CCP**)
  - Unit cell showing the full symmetry of the arrangement is Face-Centred *Cubic*
    - Cubic: $a = b = c$, a = b = g = 90°
    - 4 atoms in the unit cell: (0, 0, 0) (0, $^1/_2$, $^1/_2$) ($^1/_2$, 0, $^1/_2$)

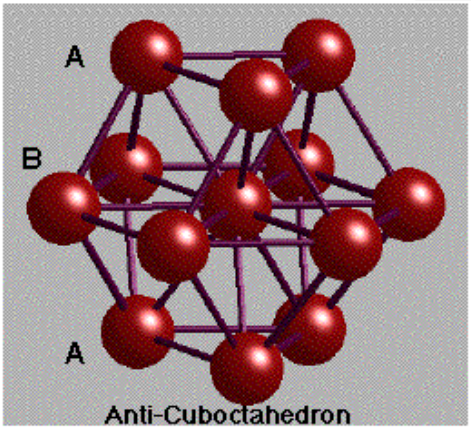
($^1/_2$, $^1/_2$, 0)

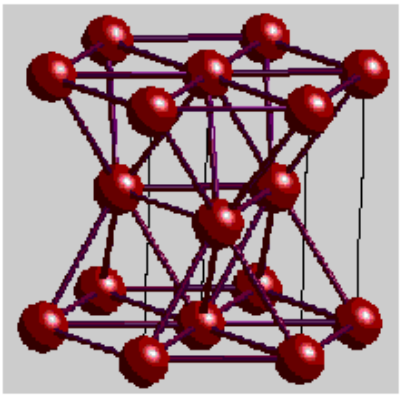


HEXAGONAL CLOSE-PACKING



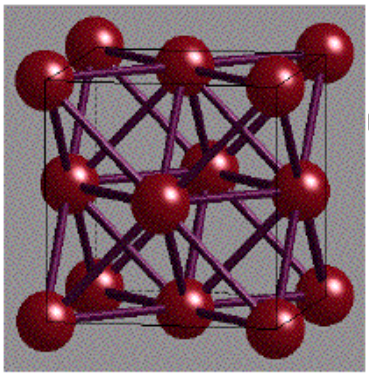




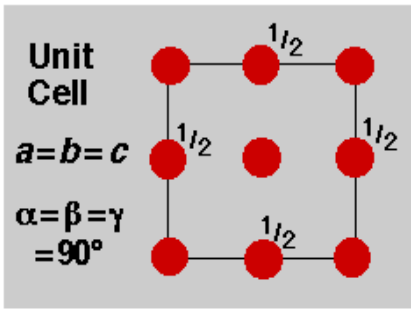


2 atoms in the unit cell (0, 0, 0) ($^2/_3$, $^1/_3$, $^1/_2$)

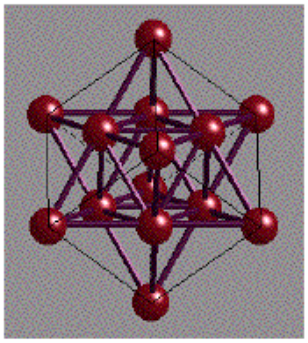
View a Quicktime HCP Movie or Quicktime HCP VR scene

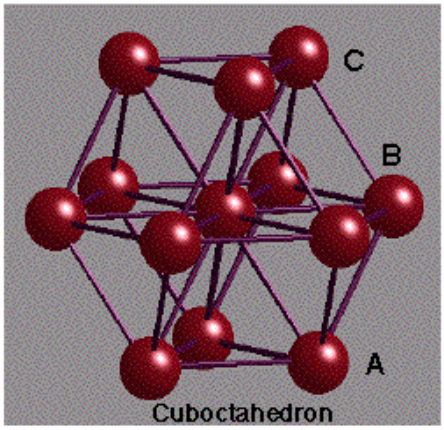


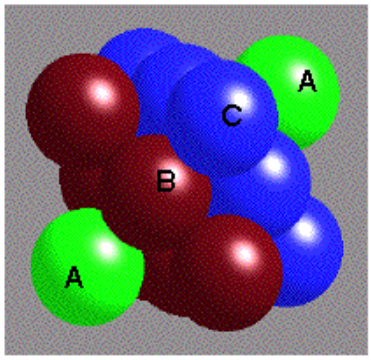
CUBIC CLOSE-PACKING



Face-Centred Cubic (FCC) Unit Cell



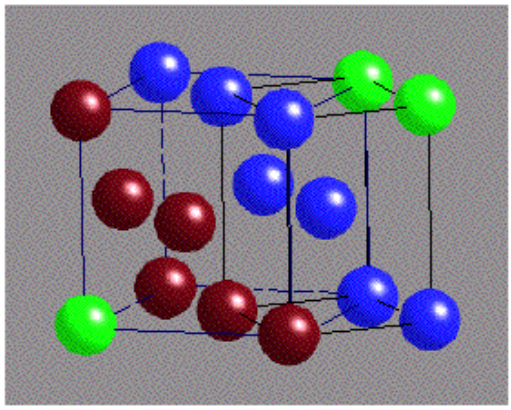




4 atoms in the unit cell (0, 0, 0) (0, $^1/_2$, $^1/_2$) ($^1/_2$, 0, $^1/_2$) ($^1/_2$, $^1/_2$, 0)

View a Quicktime CCP Movie or Quicktime CCP VR scene

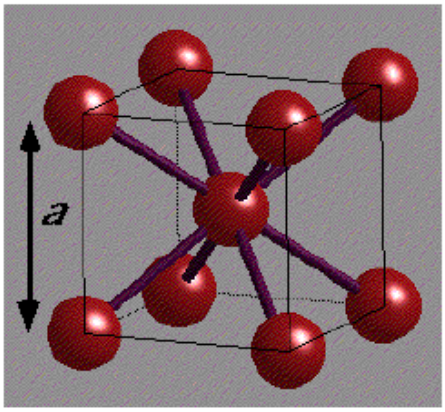
A smaller (2 atoms per cell) **body-centred TETRAGONAL Unit Cell** can be found *but doesn't show the full symmetry of CCP in the way the FCC Cell does*

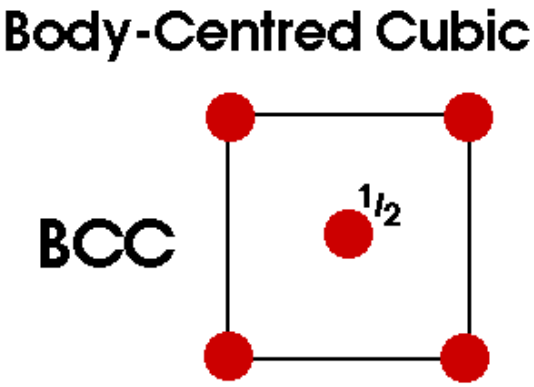


The most common close-packed structures are

METALS

A NON-CLOSE-PACKED structure adopted by some metals is:-





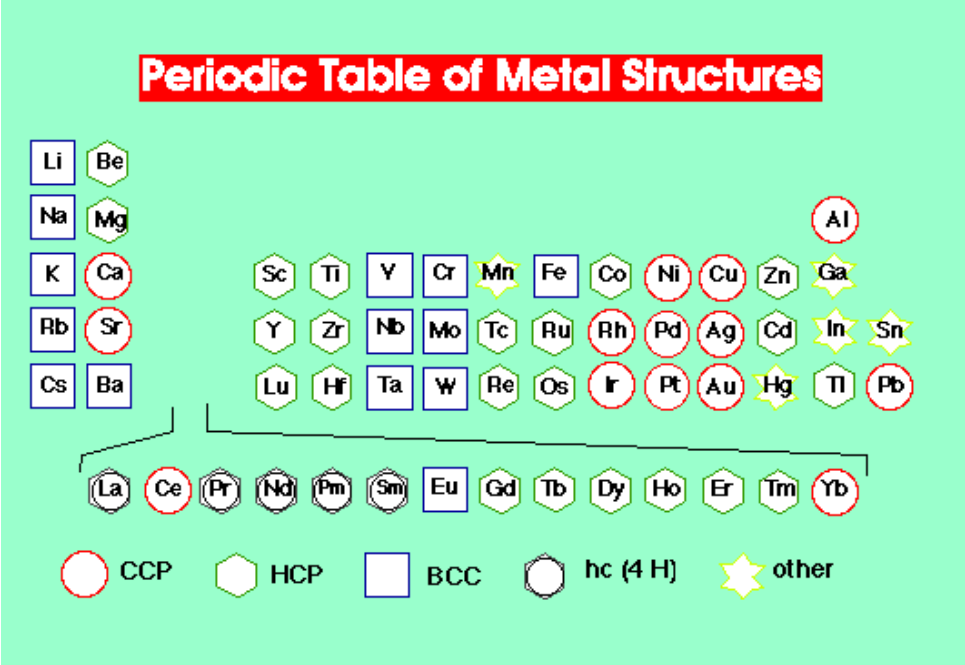
View a Quicktime BCC Movie or Quicktime BCC VR scene

68% of space is occupied

Coordination Number ?

8 Nearest Neighbours at 0.87*a*

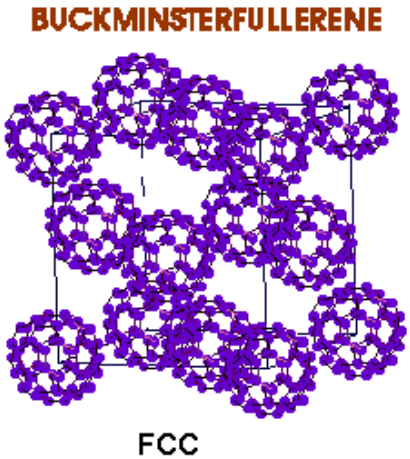
6 Next-Nearest Neighbours at 1*a*



- **Polymorphism:**
  - Some metals exist in different structure types at ambient temperature & pressure
  - Many metals adopt different structures at different temperature/pressure
- Not all metals are close-packed
- *Why different structures?*
  - residual effects from some **directional effects** of atomic orbitals
- Complex to predict structures
  - **BCC** clearly adopted for ***low number*** of valence electrons
  - Best explanations are based on **Band Theory** of Metals
    - Initially applied by Coulson & Hume-Rothery in Oxford
    - Still actively researched in Oxford by Prof. D.G. Pettifor using Density Functional Theory (DFT). See his book "*Bonding & Structure of Molecules & Solids*", OUP, 1995
  - In cases of polymorphism **BCC** is the structure adopted at ***higher temperatures***
- **More Complex close-packing sequences** than simple HCP & CCP are possible
  - HCP & CCP are merely the simplest close-packed stacking sequences, others are possible!
    - All spheres in an HCP or CCP structure have **identical** environments
  - Repeats of the form **ABCB**.... are the next simplest

        - There are **two** types of sphere environment
            - surrounding layers are both of the same type (*i.e.* **anti-cuboctahedral** coordination) like HCP, so labelled **h**
            - surrounding layers are different (*i.e.* **cuboctahedral** coordination) like CCP, so labelled **c**
        - Layer environment repeat is thus **hchc**...., so labelled **hc**
        - ***Unit cell*** is alternatively labelled **4 H**
            - Has **4 layers** in the *c*-direction
            - **Hexagonal**
        - The **hc (4 H)** structure is adopted by early lanthanides
    - Samarium (Sm) has a 9-layer **chh** repeat sequence
- **Non-Ideality** of Structures
    - Cobalt metal that has been cooled from T > 500°C has a close-packed structure with a **Random stacking sequence**
    - "Normal" HCP cobalt is actually **90% AB... & 10% ABC**... - *i.e.* non-ideal HCP
    - Many metals deviate from perfect HCP by "**Axial Compression**"
        - *e.g.* For Beryllium (Be) $^{c}/_{a}$ = 1.57 (*c.f.* ideal $^{c}/_{a}$ = 1.63)
        - Coordination is now [6 + 6] with slightly shorter distances to neighbours in adjacent layers

- Other Systems may be Classified as having Similar Structures



CrystalMaker file for C_{60}

Further information about Fullerenes

Location of Interstitial Holes in Close-Packed Structures

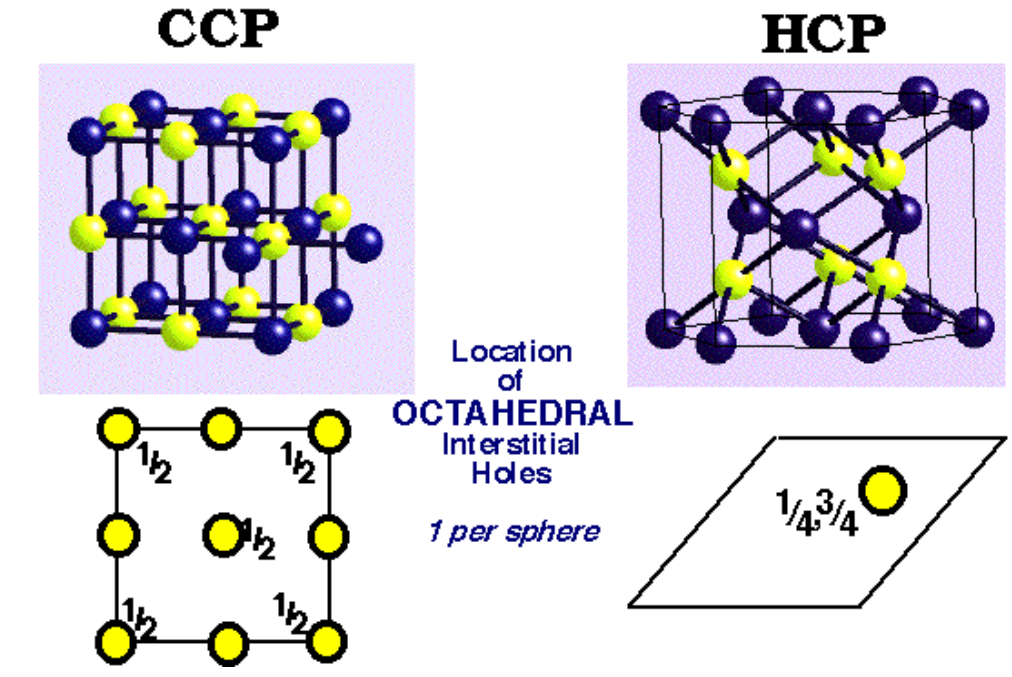
The HOLES in close-packed arrangements may be filled with atoms of a different sort.

It is therefore important to know:-

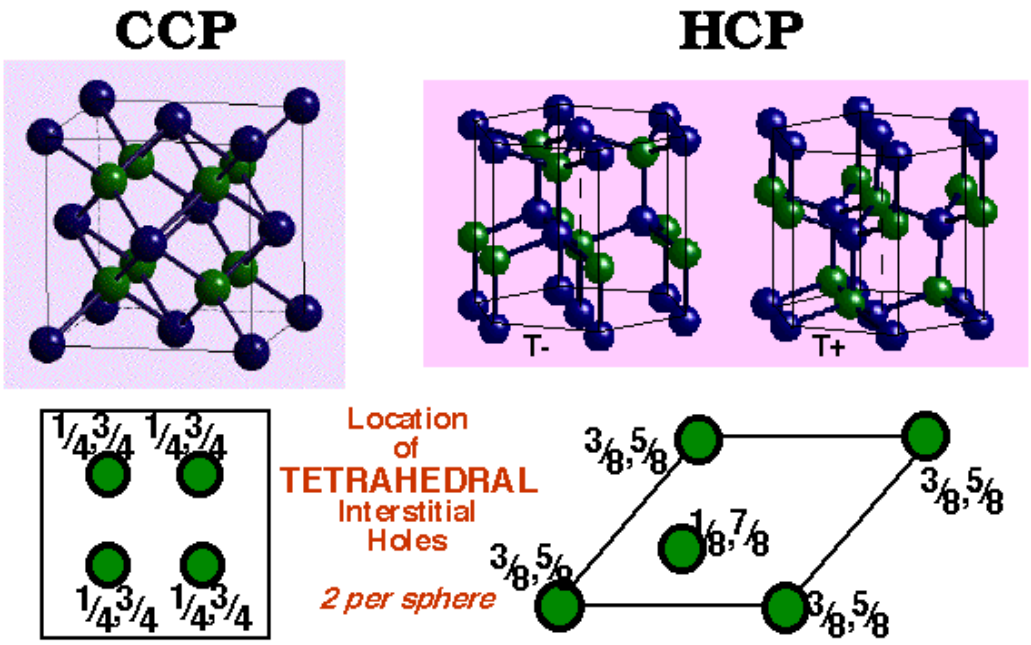
- How holes are displaced in space relative to the positions of the spheres
- How holes are displaced relative to each other

The hole positions are shown relative to the unit cells below

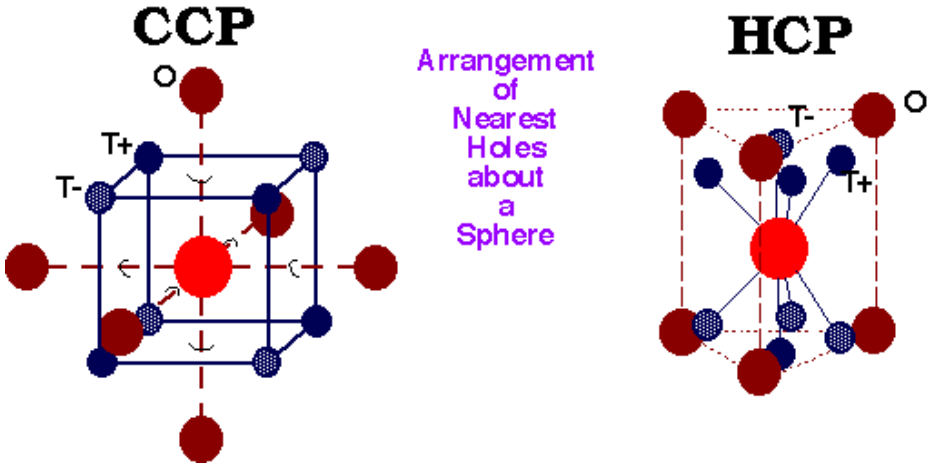
The structures possible from filling them are considered in Lecture 2



CCP Octahedral holes----------HCP Octahedral holes



CCP Tetrahedral holes----------HCP Tetrahedral holes



Solids Page Lecture 1 Lecture 2 Lecture 3 Lecture 4 Problems Set Help

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