Structural Inorganic Chemistry

Molecular *v.* extended solids

Types of solids

- crystalline,
  long range order (>10^3 atoms)

- amorphous,
  short range order (~ 100 Å)

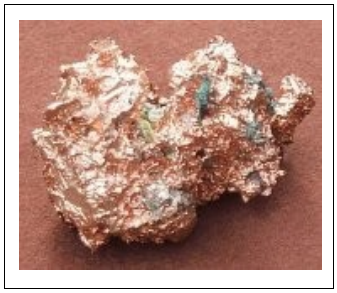
special type :glass, characterised by the glass transition temperature, T_g

Crystalline

- ionic
  NaCl

- covalent
  diamond, SiC

- metallic
  Cu, fcc



Inorganic structures

Ionic model

- electrostatic forces between ions
- close packing of ions
- ions as hard spheres

Coulombs law

$$F = \frac{1}{4\pi\epsilon_0} \cdot \frac{Q_1 Q_2}{r^2}$$

Electrostatic energy

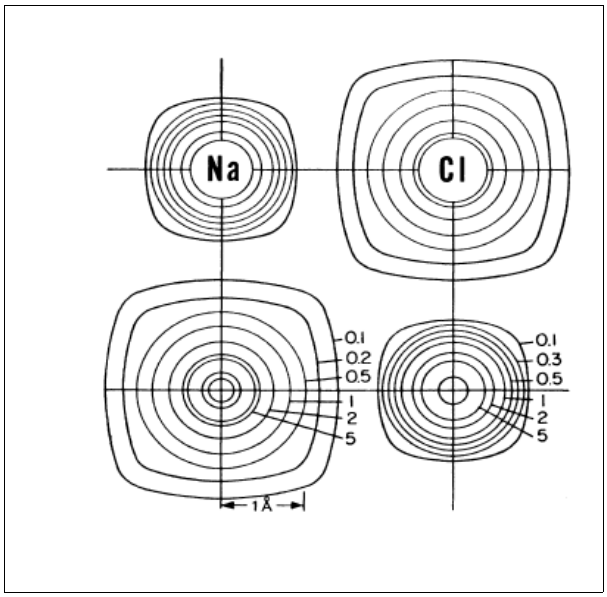
$$U = \frac{1}{4\pi\epsilon_0} \cdot \frac{Q_1 Q_2}{r}$$

Hence close packing

Ions as hard spheres

Closed "shells" np^6

Electron density map from x-ray diffraction of NaCl



Witte and Wölfel
Rev. Mod. Phys 30, 51 (1958)

Building up inorganic structures

Two ideas

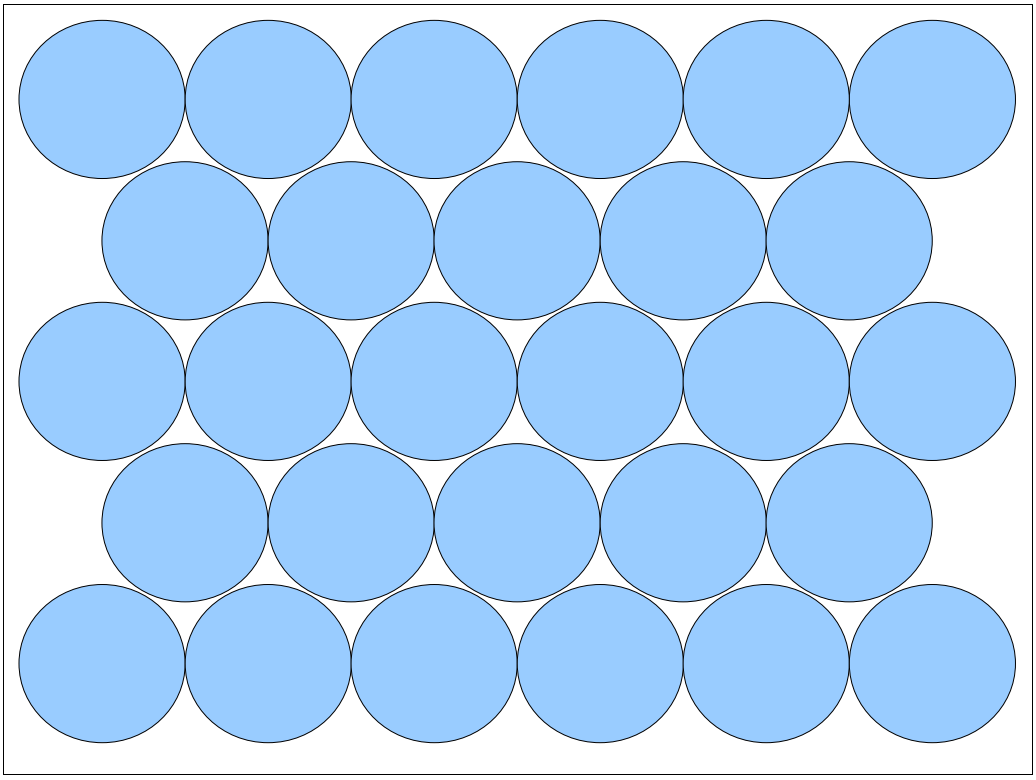
- closed packed layers of spheres
  occupy 74% of space

- filling of interstitial sites

Excellent descriptive value

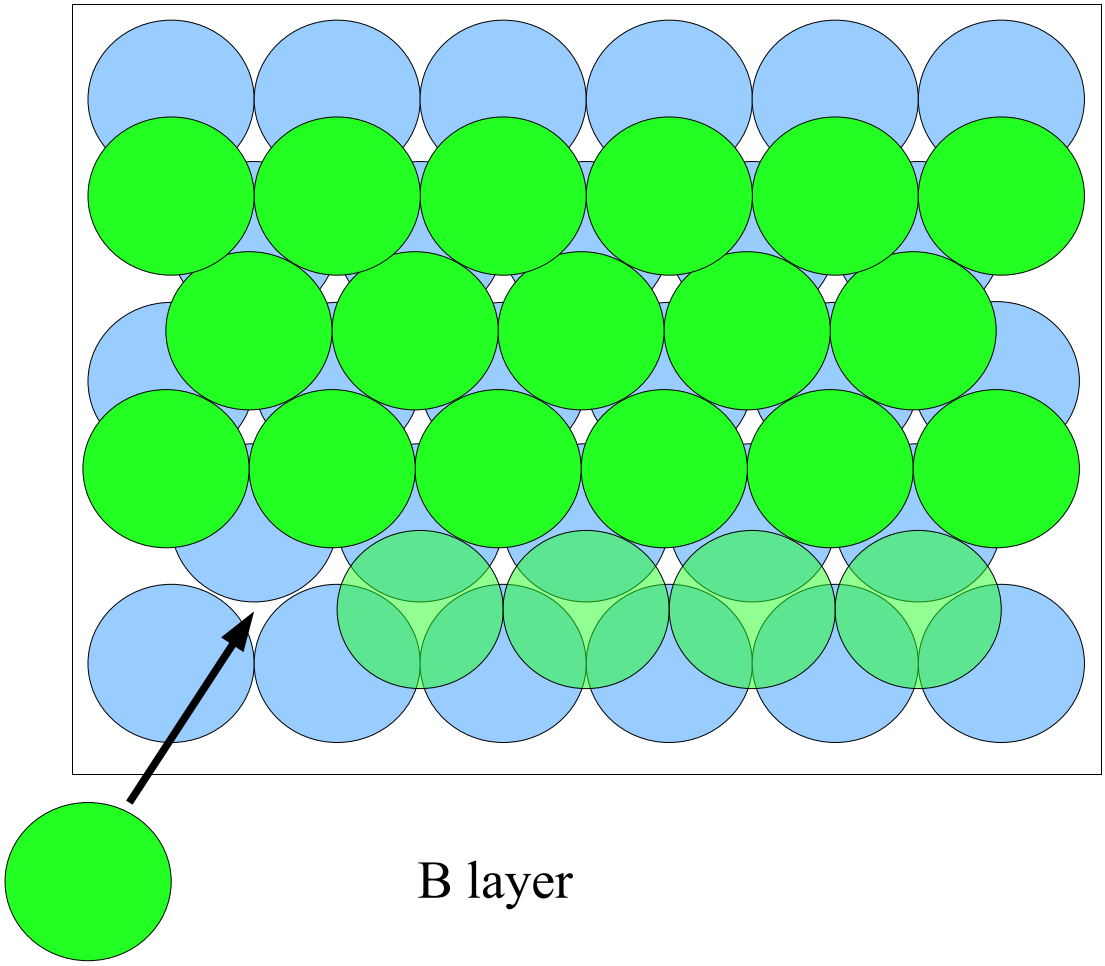
Limited predictive use

First layer



A layer

Second layer

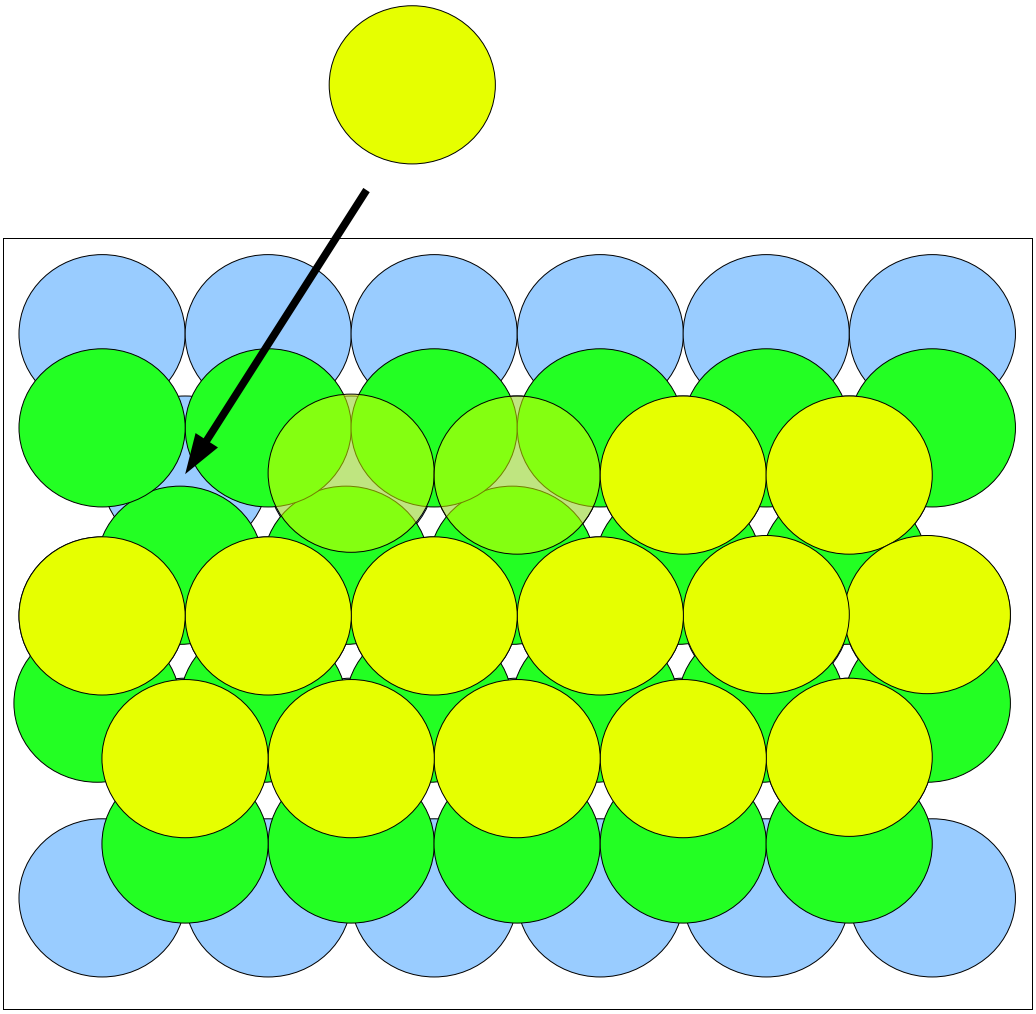


B layer

Third layer

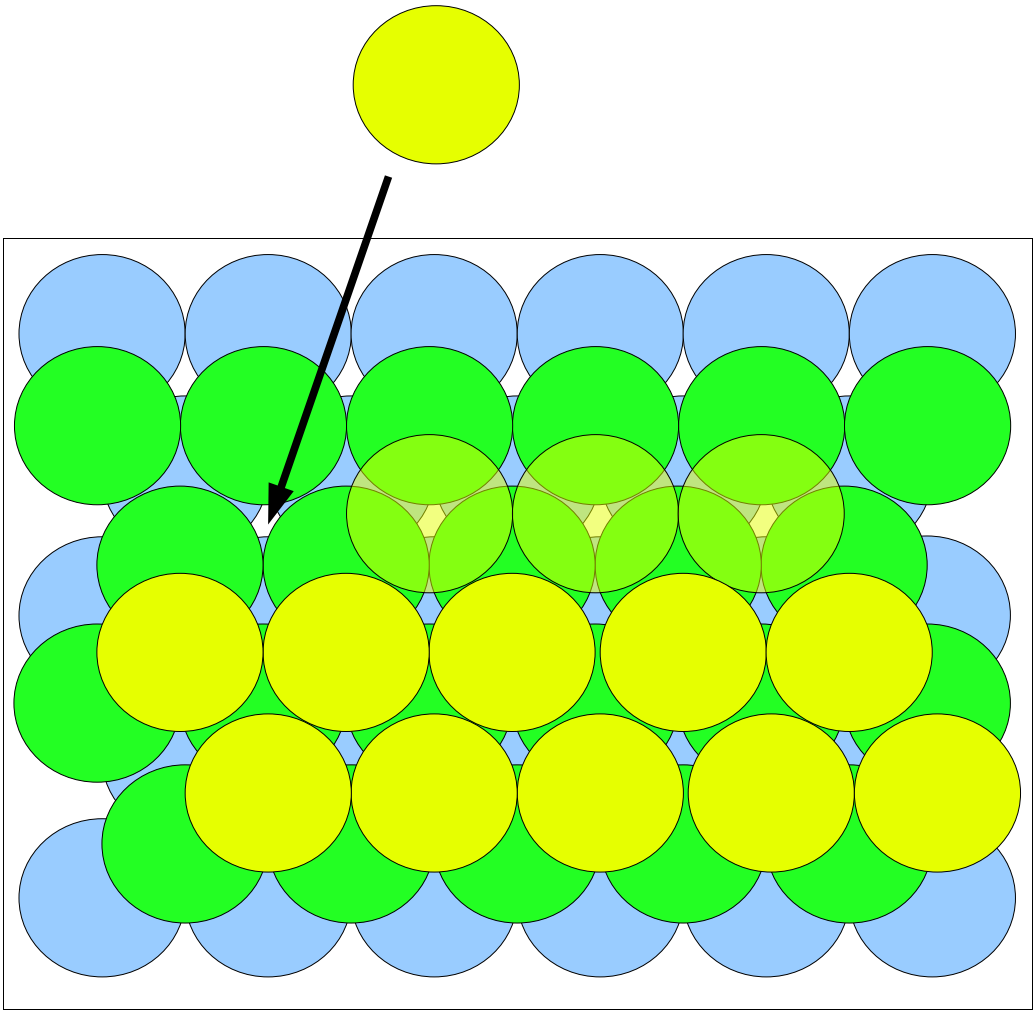
Two possibilities

Above original A layer



AB AB AB AB
Hexagonal close packing, hcp

Above holes common to A and B layers



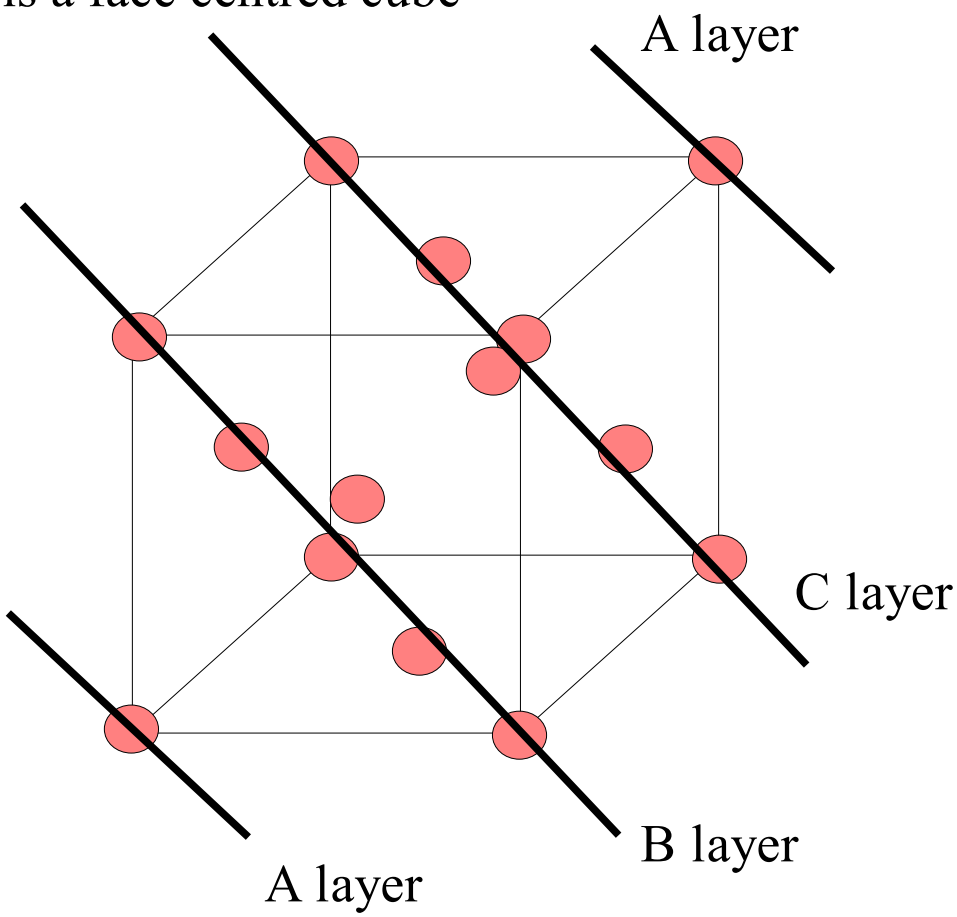
C layer

ABC ABC ABC
Cubic close packing, ccp

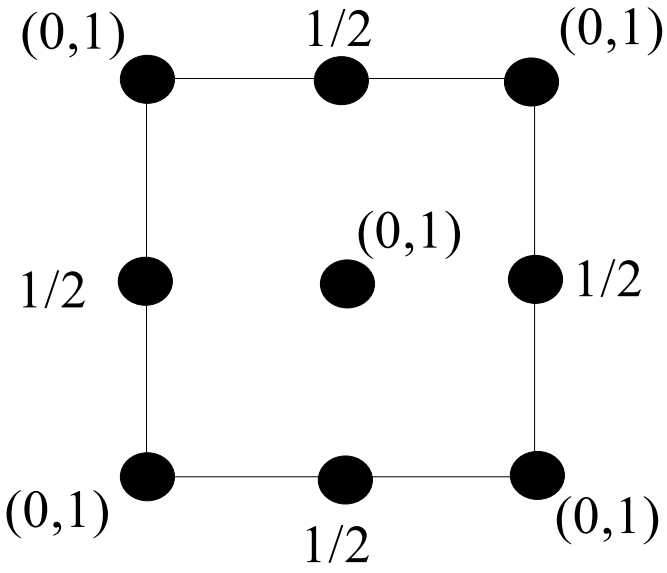
Relationship between close packing and unit cell

Cubic close packing

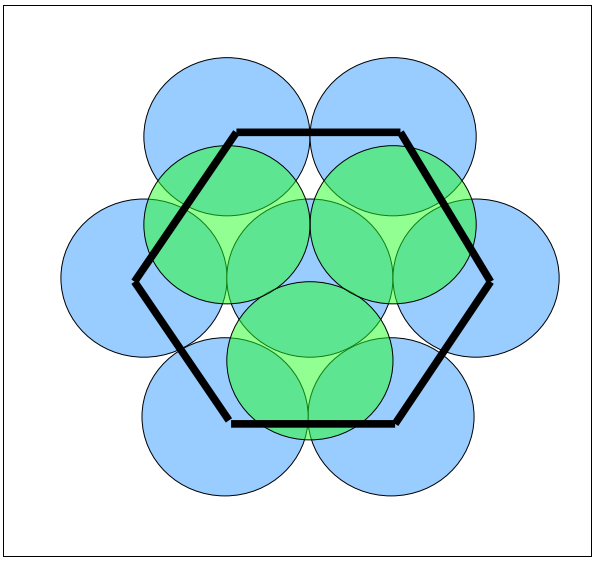
Unit cell is a face centred cube



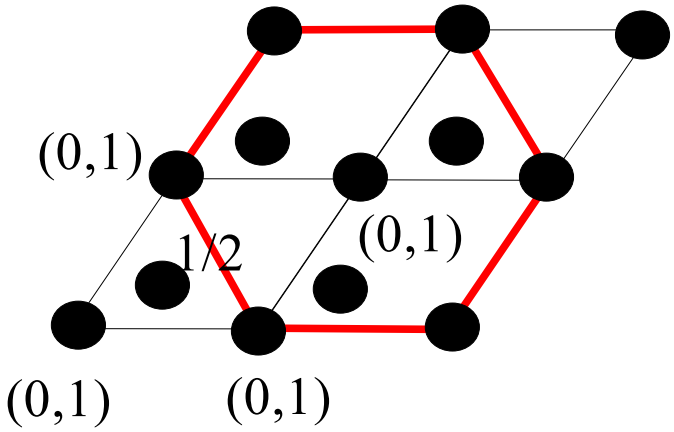
Orthographic projection of the unit cell



Hexagonal close packing



Orthographic projection

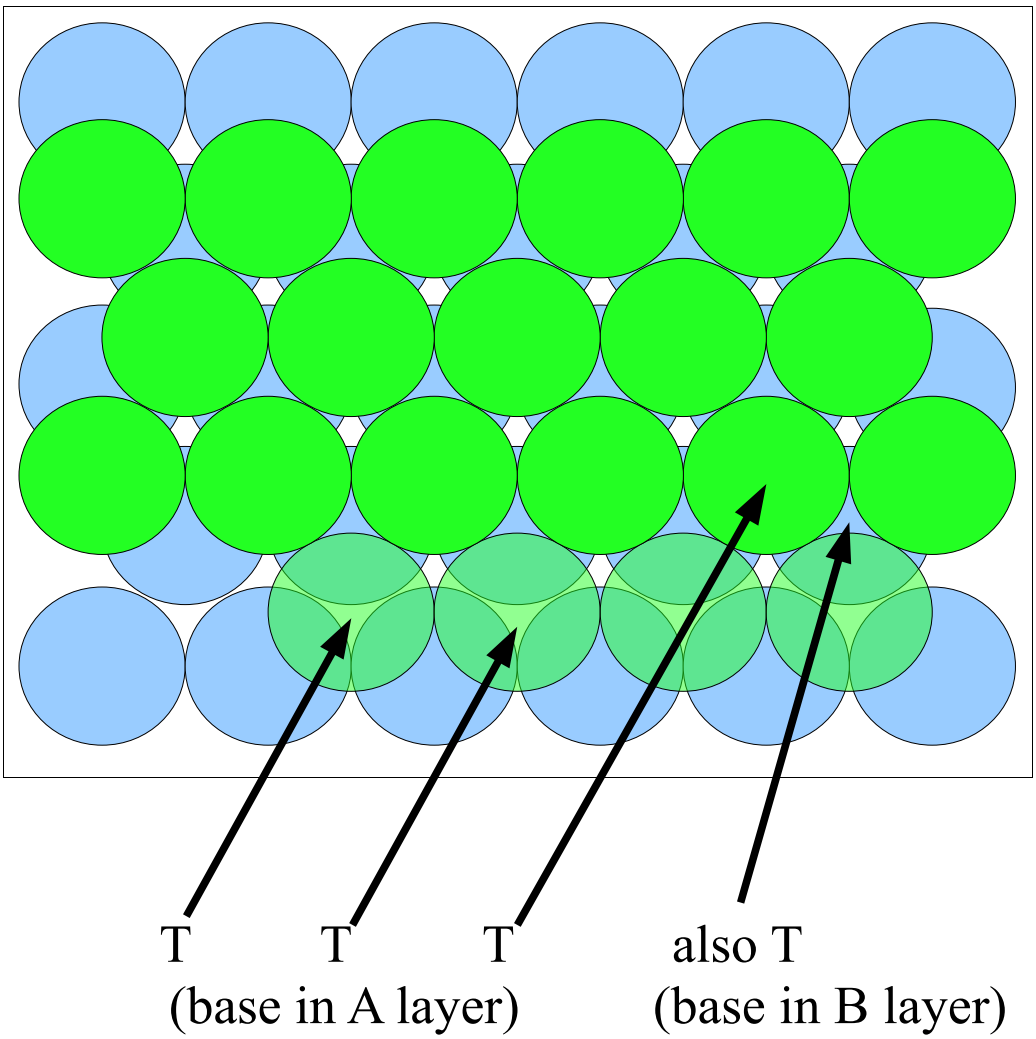


Unit cell has atom positions labelled

Interstitial sites

Tetrahedral

Between two layers AB, or BA, BC and CB

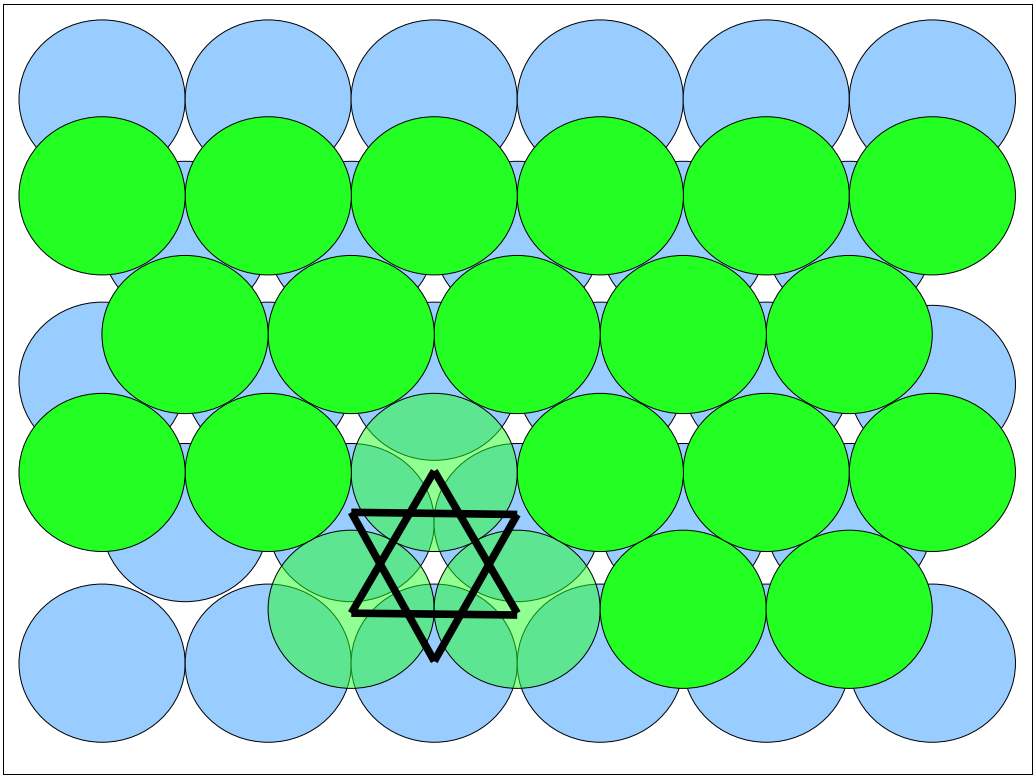


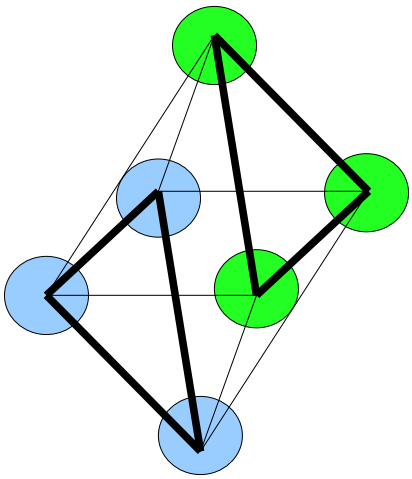
Two sites for every close packed ion.

Octahedral

Between two layers AB, or BA, BC and CB

Harder to spot





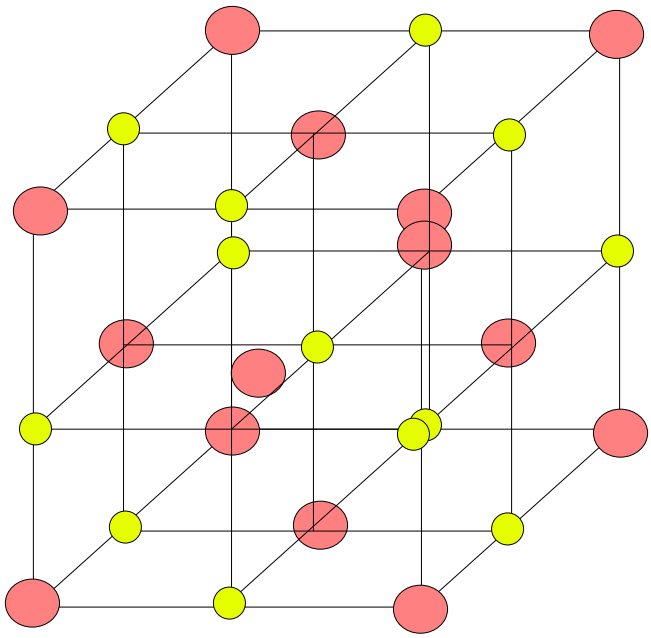
One for each close packed ion

Structures

Type and fraction	ccp	hcp
All tetrahedral	Fluorite, CaF_2	(not known)
All octahedral	Rock salt, NaCl	Nickel arsenide NiAs
½ tetrahedral	Zinc blende, ZnS	Wurtzite, ZnS
½ octahedral	$CdCl_2$	CdI_2

Rock salt structure

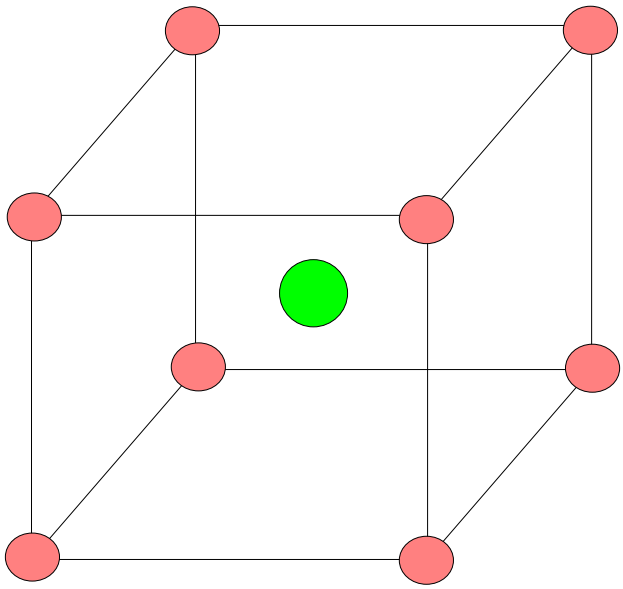
Interpenetrating fcc



NB

Caesium chloride structure

Not close packed, occupies 68% of space



Not body centred cubic

Definitions

Unit cell
The smallest repeating unit which shows the full symmetry of the crystal structure. Translates it to build up the entire structure

Asymmetric unit
Smallest collection of atoms which can be used to generate the entire structure when the symmetry operations contained within the space group are applied

Space group
A three dimensional point group: Add elements of translation to the point group. Also contains the elements:

rotation + translation = screw axis
mirror + translation = glide plane

Combine 32 point groups with these elements gives 230 space groups

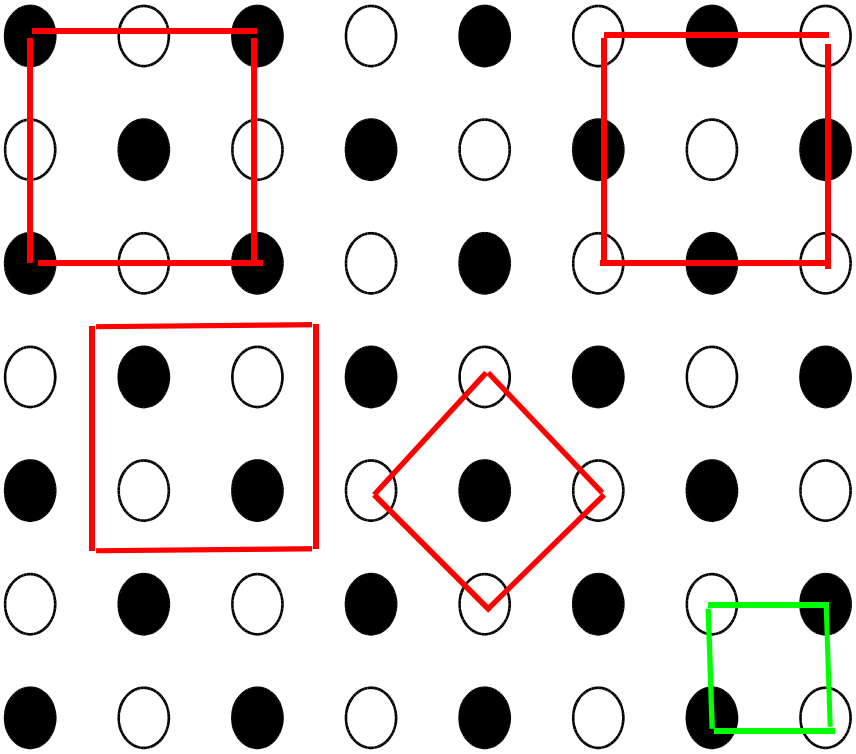
Point group
A collection of symmetry elements obeying the mathematical axioms of a group: closure, identity, associative, inverse. 32 groups in all

- rotation axes 1,2,3,4 and 6
- inversion axes $\bar{1}$,$\bar{2}$,$\bar{3}$,$\bar{4}$ and $\bar{6}$
- mirror plane, *m*

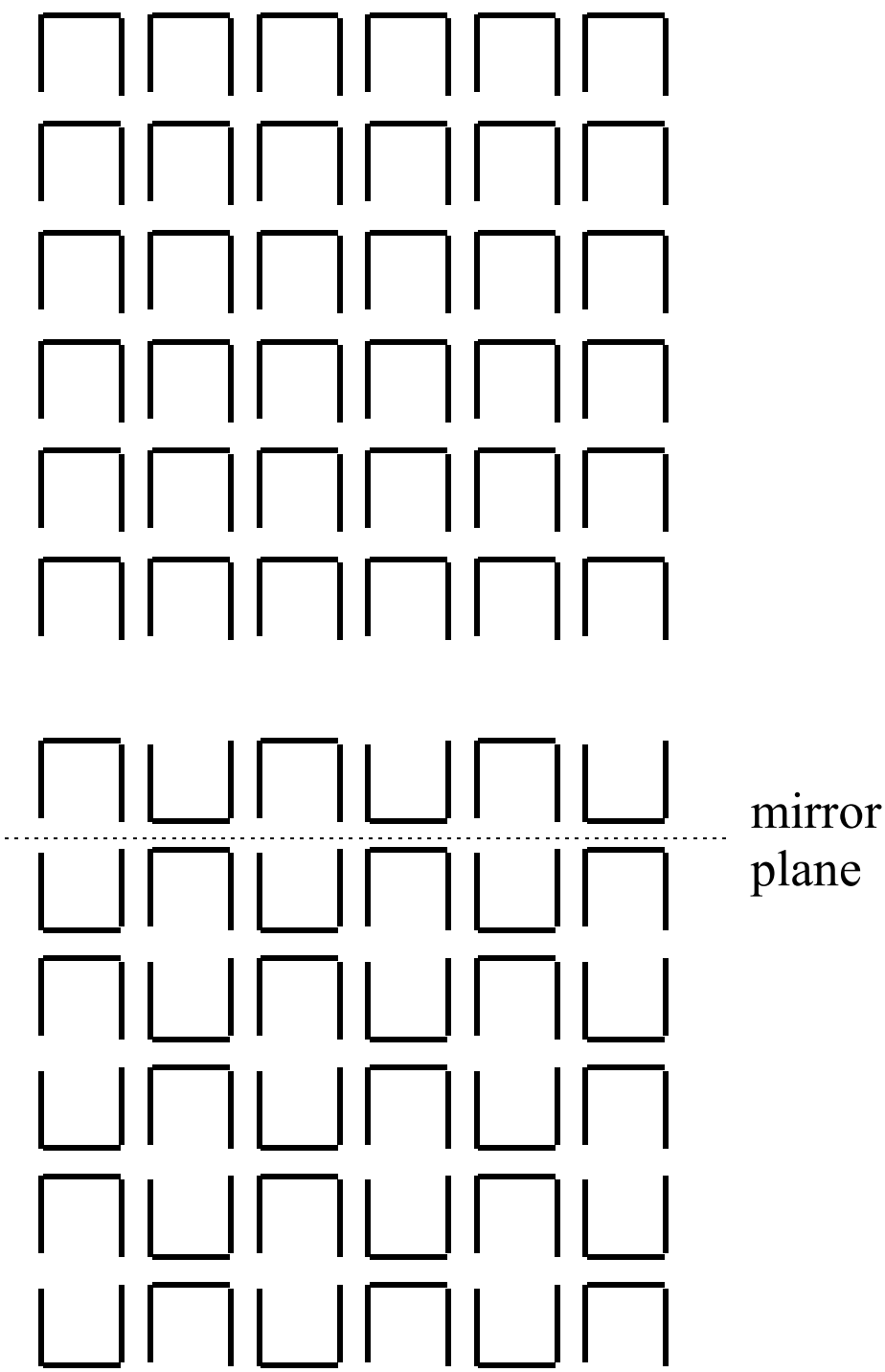
Note the absence of a fivefold rotation axis.

Unit Cell

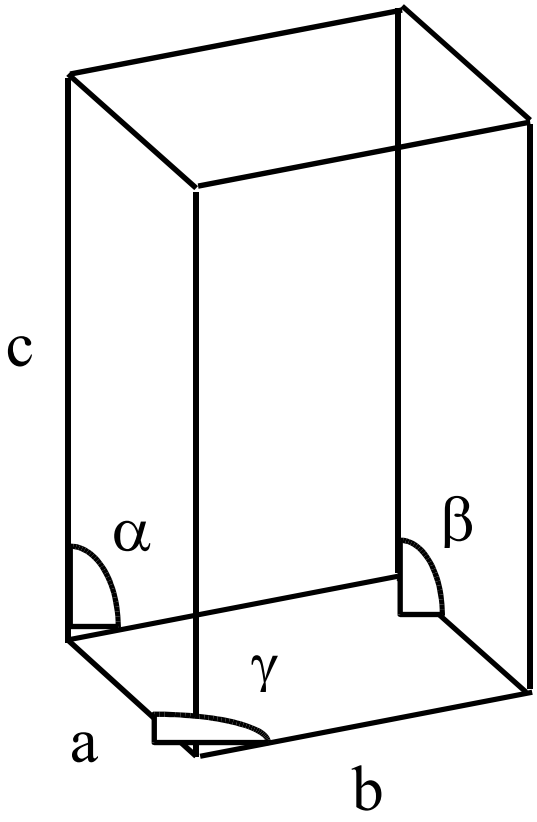
red = correct unit cells
green = incorrect



Aymmetric unit



Lattice parameters

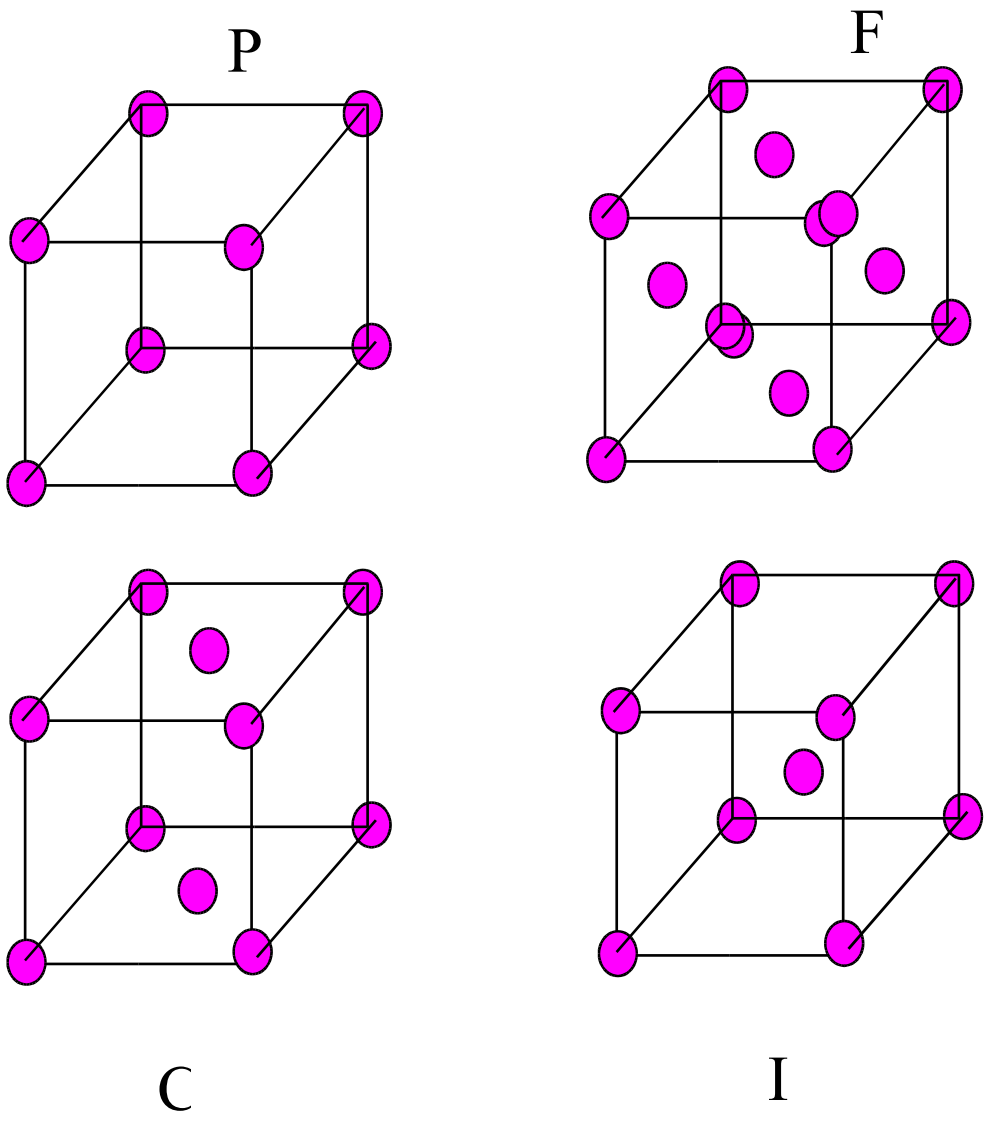


Crystal classes

triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma$
monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^o \neq \beta$
orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^o$
tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^o$
cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^o$
hexagonal	$a = b \neq c$	$\alpha = \beta = 90^o$ $\gamma = 120^o$
trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90^o$

Basic types of Cells

Primitive - contains only one lattice point



Only 14 combinations of crystal class and lattice type

Bravais lattices