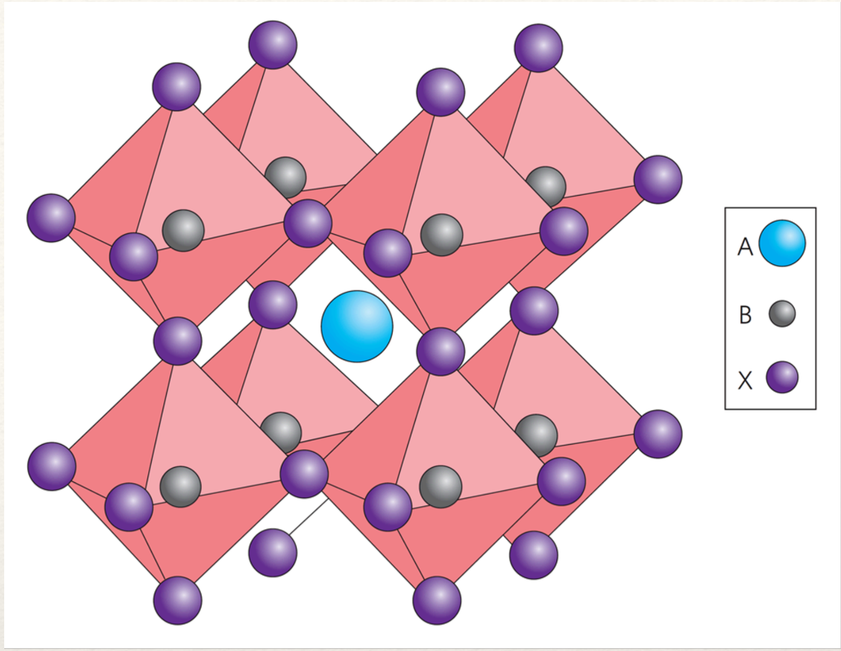

Structure of Solids - Common crystal structures

Lecture 8

CHM 637
Chemistry & Physics of Materials

Varadharajan Srinivasan
Dept. Of Chemistry
IISER Bhopal

Lecture Plan

- *Strukturberichte* structures
- Close packing of hard spheres
- Linked polyhedra
- Radius ratio and stability

Strukturberichte Structures

Topologically identical structures can be grouped together into one type for ease of their description.

The base structures for these different types are often minerals and elemental solids which are found in nature.

One such classification was used by *Zeitschrift fur Kristallographie* in the catalogue of crystal structures *Strukturberichte* Vol. 1, published in 1920. The classification assigned symbols to the structure types called *Strukturberichte* symbols.

For more complex structures the base mineral names are used instead of the symbols.

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Strukturberichte Structures

Unit cells are described by specifying

- The Bravais lattice type
- The lattice parameters (*a*,*b*,*c*) [and angles if needed].
- The coordinates (*x*,*y*,*z*) of the basis atoms in units of *a*, *b* and *c*, respectively.
- The space group
- Number of formula units *Z* in the cell.

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- Number of formula units Z in the cell.

Density of the crystal can be computed as

$$\rho = \frac{\sum_{i=1}^{q} n_i m_i / N_A}{V}$$

q = no. of types atoms in the unit cell
n_i = no. of atoms of type i
m_i = molar mass of type i atoms
V = volume of unit cell

Strukturberichte Structures

***A1* or Cubic close-packed structure**

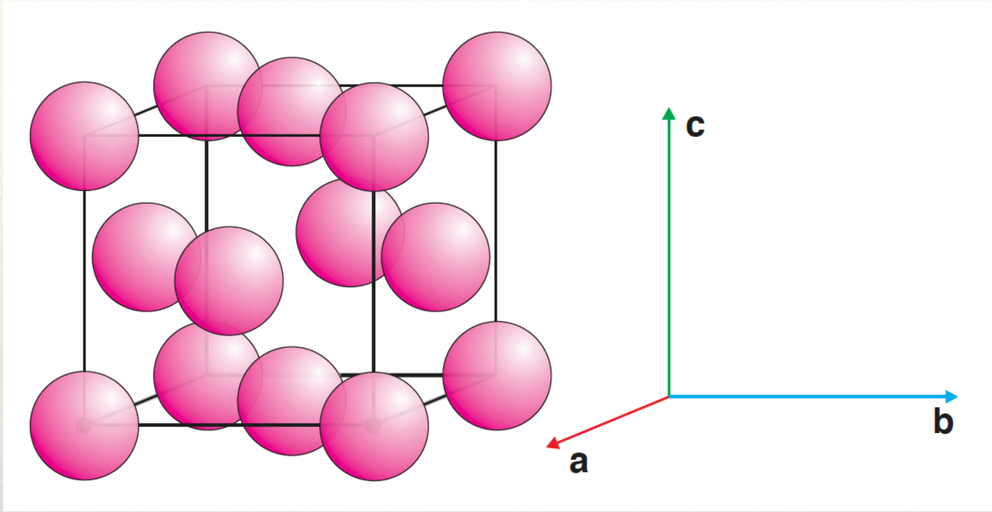
General Formula: M

Lattice: Cubic face-centred

$Z = 4$

Atom positions:

(0, 0, 0); (1/2, 1/2, 0); (0, 1/2, 1/2); (1/2, 0, 1/2)



Example, Cu (a=0.360 nm, $m = 63.546$ g/mol)

$$\rho = \frac{4 \times 63.546/N_A}{(0.360 \times 10^{-9})^3} = 9.045 \text{ g/c.c.}$$

Fraction of volume occupied as hard spheres = 0.7405

Coordination No. = 12

Other examples include noble gases, Al, Ni, Pd, Ir, Pb, Ca, Ag, Au.

Strukturberichte Structures

***A2* or Body-centred cubic structure**

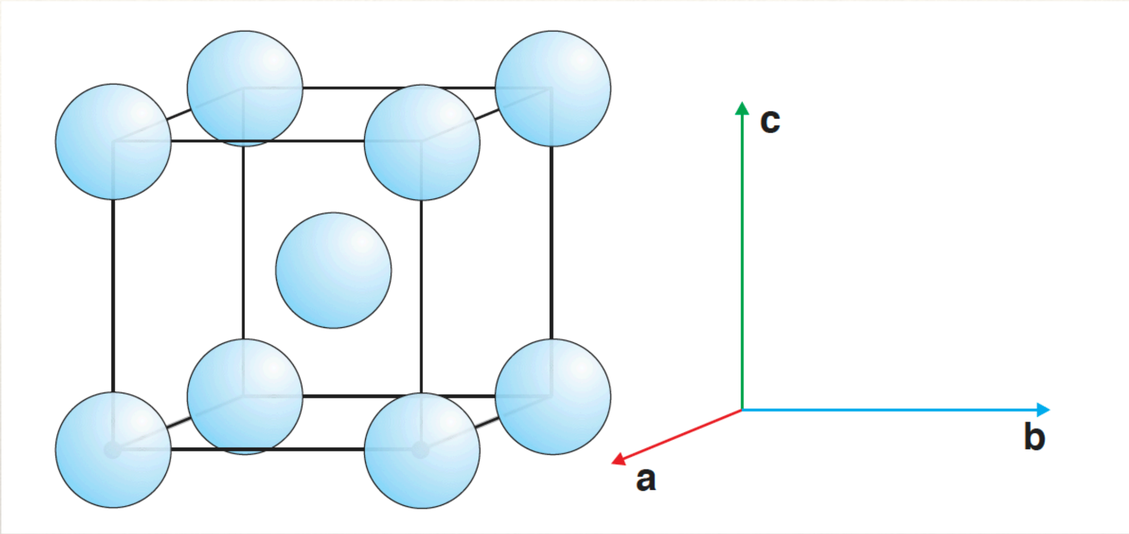
General Formula: M

Lattice: Cubic body-centred

$Z = 2$

Atom positions:

(0, 0, 0); (1/2, 1/2, 1/2)



Example, W (a=0.316 nm, $m = 183.84$ g/mol)

$$\rho = \frac{2 \times 183.84/N_A}{(0.316 \times 10^{-9})^3} = 19.34 \text{ g/c.c.}$$

Fraction of volume occupied as hard spheres = 0.6802

Coordination No. = 8

Other examples include Li, K, Cr, Rb, Ba, V, Fe, Cs, Ta.

Strukturberichte Structures

***A3* or Hexagonal structure**

General Formula: M

Lattice: Primitive hexagonal

$Z = 2$

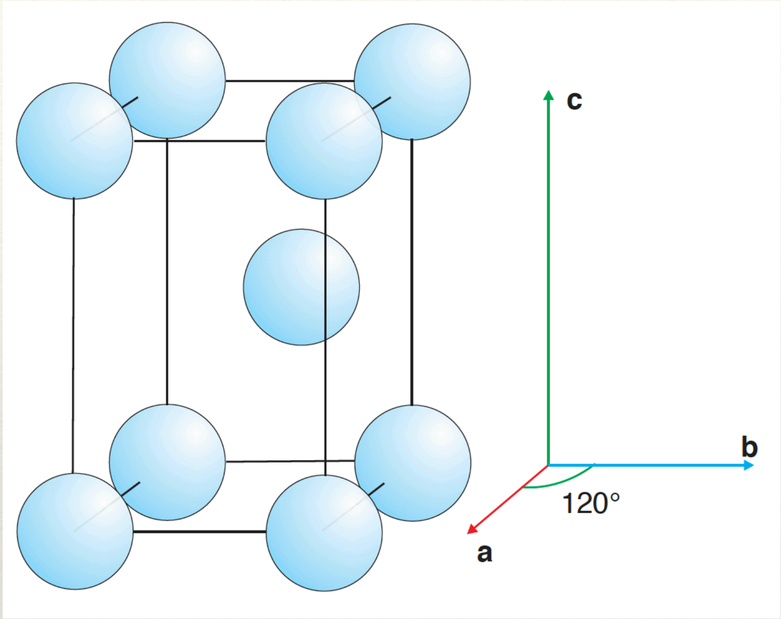
Atom positions:

(0, 0, 0); (1/3, 2/3, 1/2)

Ex., Mg (a=0.321 nm, c=0.521 nm, $m = 24.305$ g/mol)

$$\rho = \frac{2 \times 24.305/N_A}{0.5 \times 0.321^2 \times 0.521 \times 10^{-27}} = 30.07 \text{ g/c.c.}$$

Other examples include Li, K, Cr, Rb, Ba, V, Fe, Cs, Ta.



Fraction of volume occupied as hard spheres = 0.7405

Coordination No. = 12

Strukturberichte Structures

***A4* or Diamond structure**

General Formula: M

Lattice: Cubic face-centred

$Z = 8$ ($q = 2$)

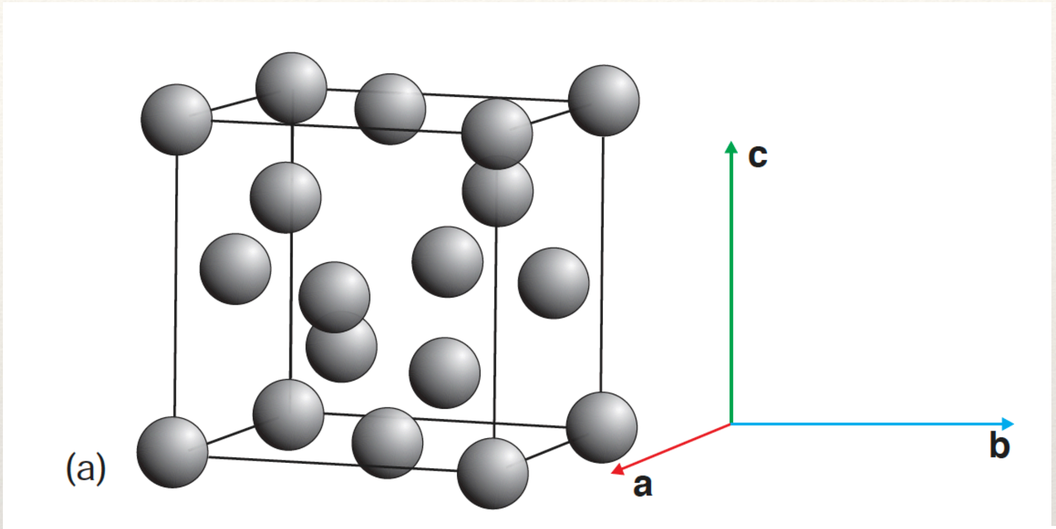
Atom positions:

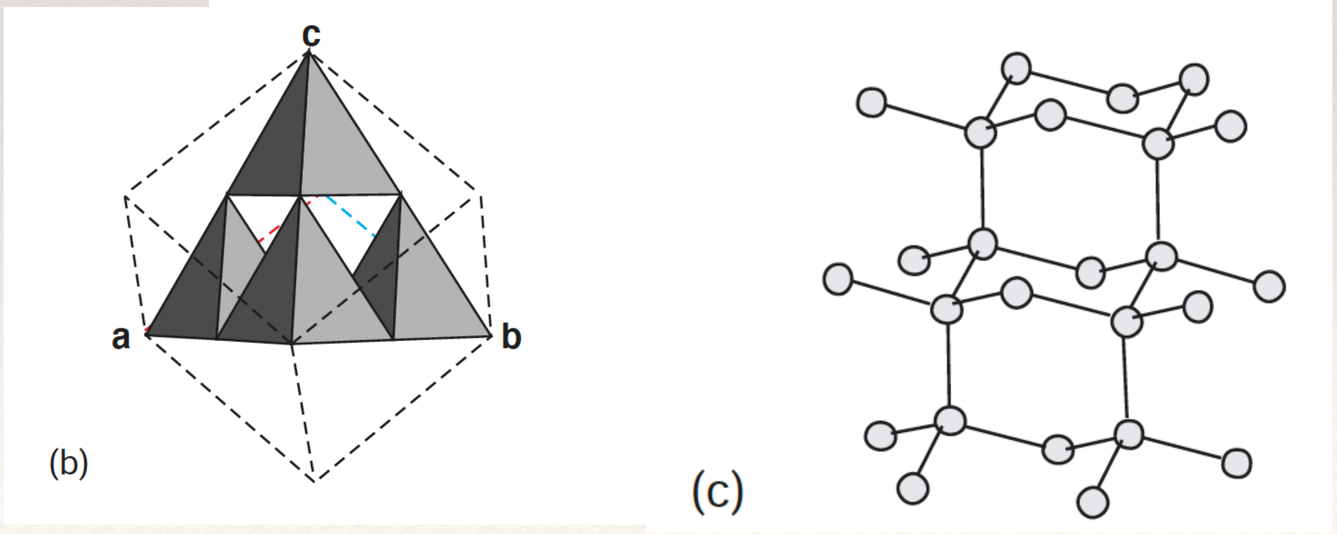
{(0, 0, 0); (1/4, 1/4, 1/4)}—> F.C.C.

Ex., C (a=0.321 nm)

Each C is surrounded by 4 other C atoms bonded to it through sp^3 bonds (0.154 nm) forming a giant molecule

Other examples: Si, Ge





Strukturberichte Structures

***A9* or graphite structure**

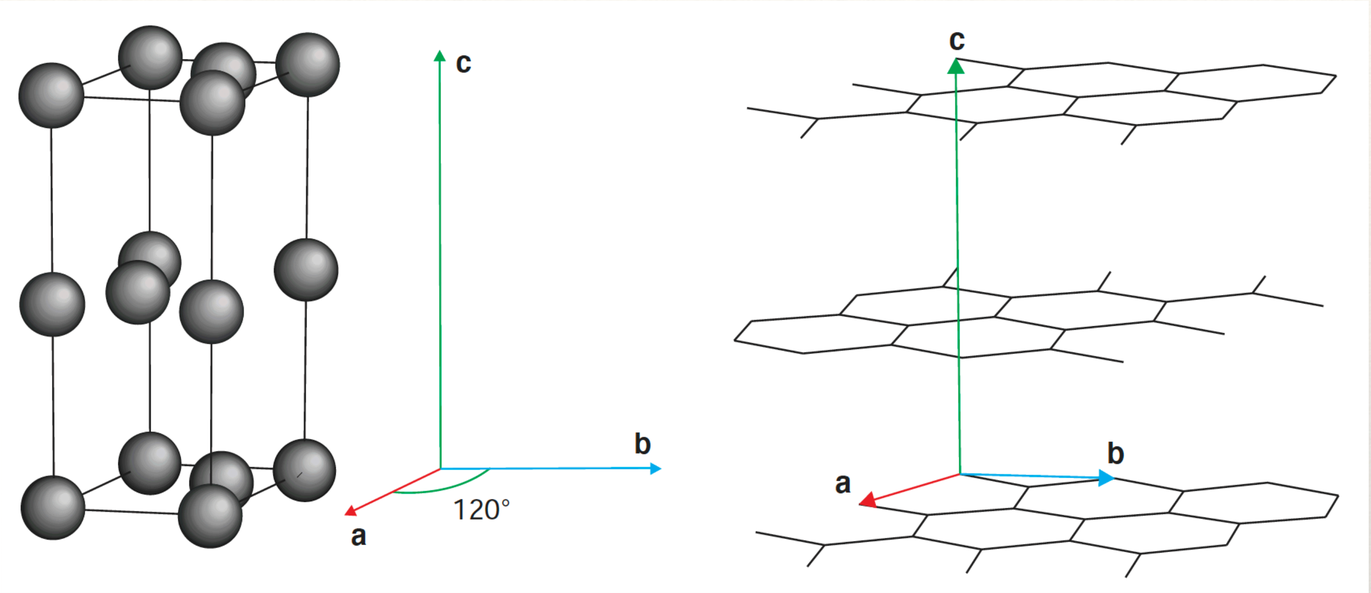
General Formula: M

Lattice: Primitive hexagonal

Z = 4

Atom positions:

(0, 0, 0); (0, 0, 1/2); (1/3, 2/3, 0); (2/3, 1/3, 1/2)



Ex., C (a=0.246 nm, c=0.671nm)

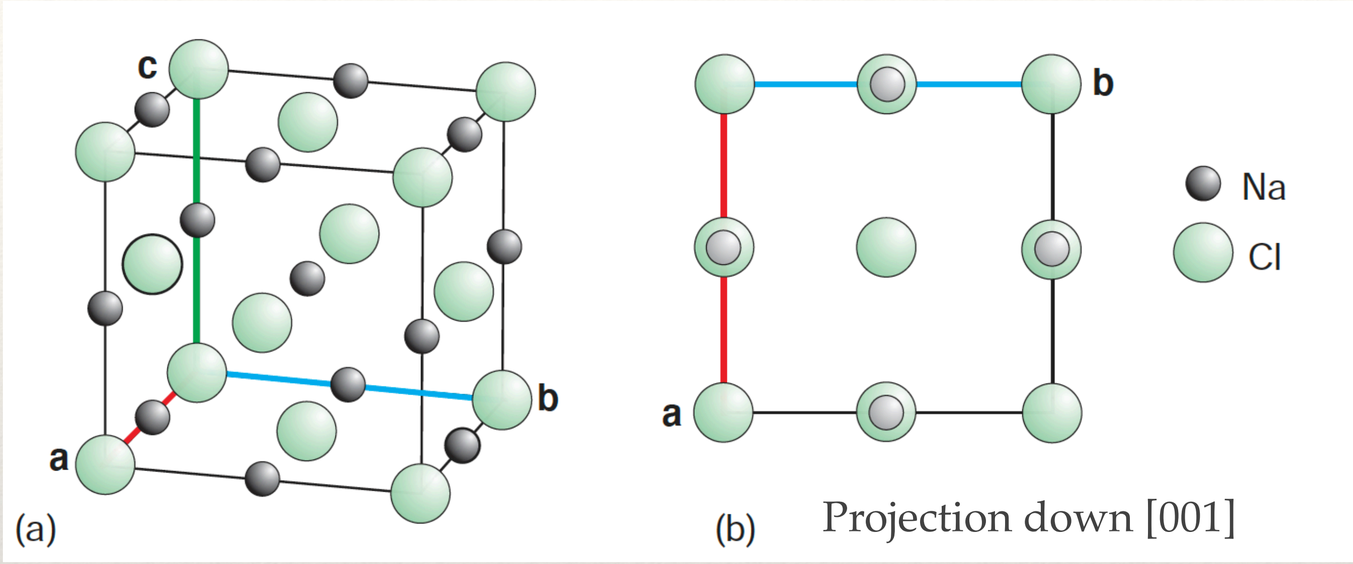
2-D sp^2 bonded sheets stacked and interacting *via* weak VW forces.

Graphene = exfoliated single sheets

An entire class of interesting 2-D materials emerge from this kind of structure.

Strukturberichte Structures

***B1* or *Halite* (Rock Salt) structure**
General Formula: MX
Lattice: cubic face-centred
$Z = 4$
Atom positions:
{M : (0, 0, 0); X: (1/2, 1/2, 1/2)}



Ex., NaCl (a=0.563 nm)

Coordination No. : 6

Density = 2.333 g/c.c.

Other examples, KCl, KBr, AgBr, PbS, NiO, MgO, MnO, LiH

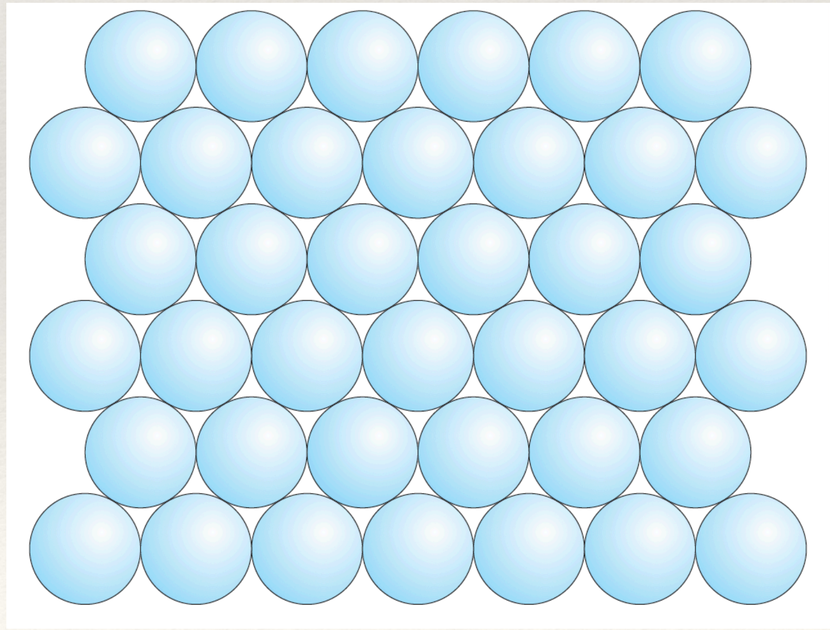
Close packing of hard spheres

We can also describe crystals in terms packing of ions imagined as hard spheres.

2 main close packing arrangements are commonly used:

1) Cubic close-packing (ccp)
2) Hexagonal close-packing (hcp)

Both are built up by stacking layers of hexagonally tiled spheres.



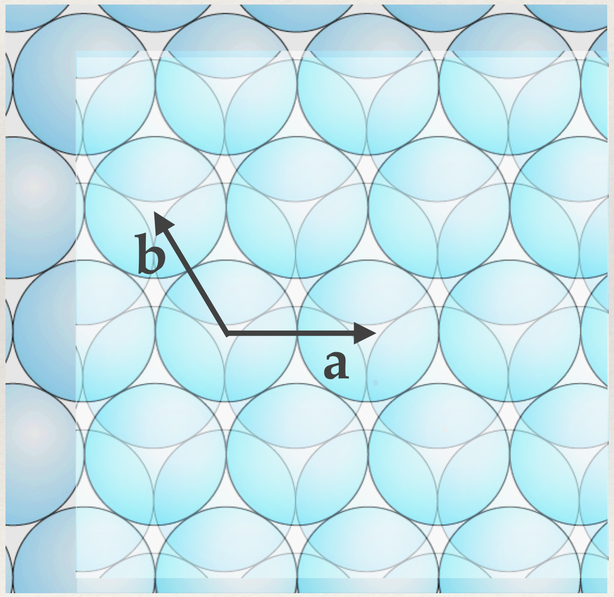
Close packing of hard spheres

Hexagonal close-packing

The second layer is placed with spheres sitting in the hollows of the first layer.

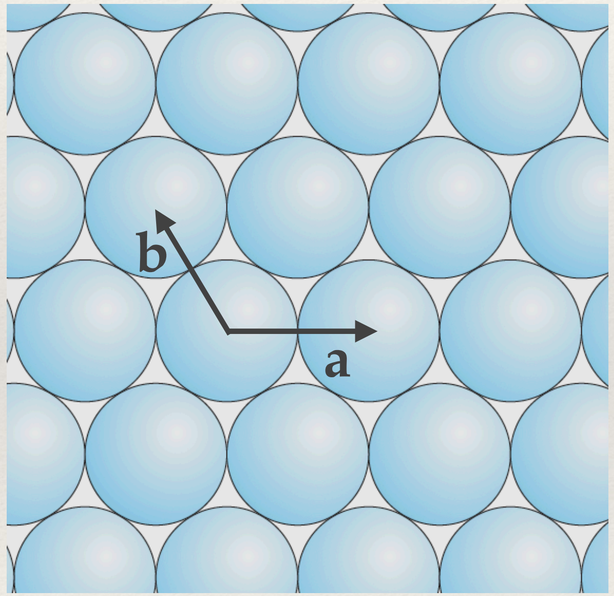
The third layer is then placed with spheres sitting on top of the spheres in the first layer.

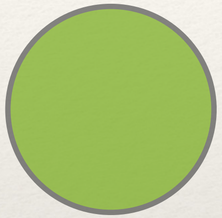
This stacking repeated indefinitely gives rise to an *ABAB*… stacking.

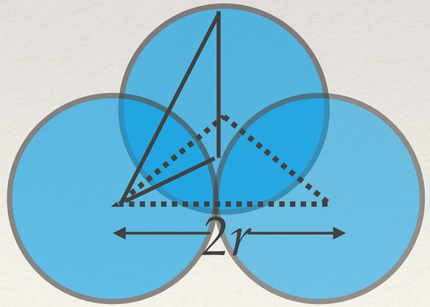


Close packing of hard spheres

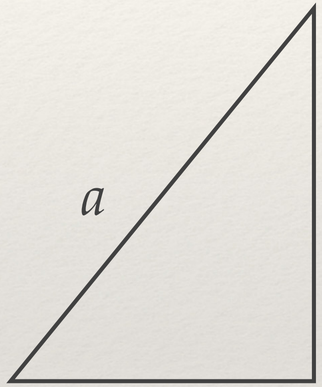
Hexagonal close-packing







$$a = b = 2r$$



$$d = \sqrt{a^2 - \left(\frac{a}{\sqrt{3}}\right)^2}$$

$$\approx 1.633r$$

Spacing between layers

Now, $c=2d$

$\Rightarrow c/a=1.633$

The structure is the same as *A3* but *c*/*a* value often deviates from the ideal value

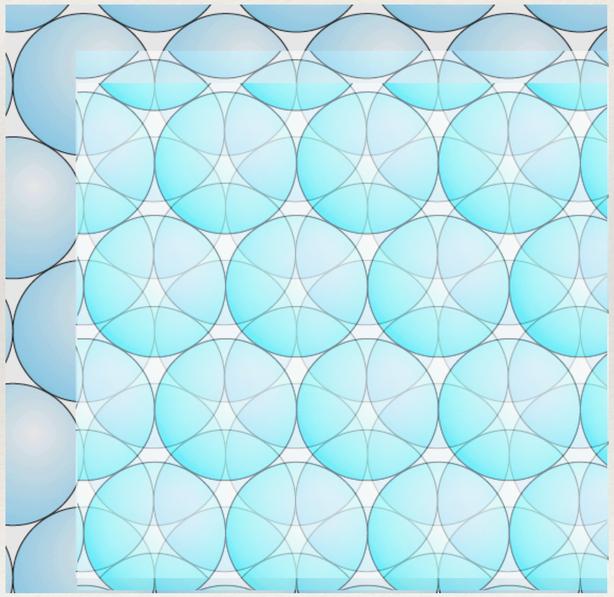
Close packing of hard spheres

Cubic close-packing

The second layer is placed with spheres sitting in the hollows of the first layer.

The third layer is then placed with spheres sitting in the hollows of the second layer.

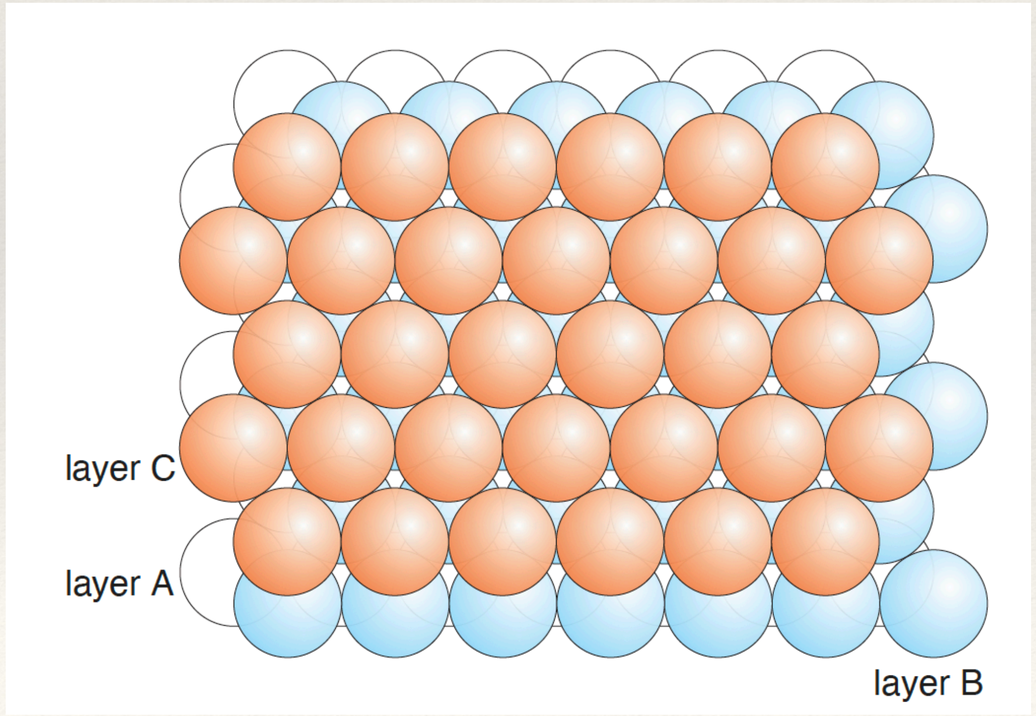
This stacking repeated indefinitely gives rise to an *ABCABC*… stacking.

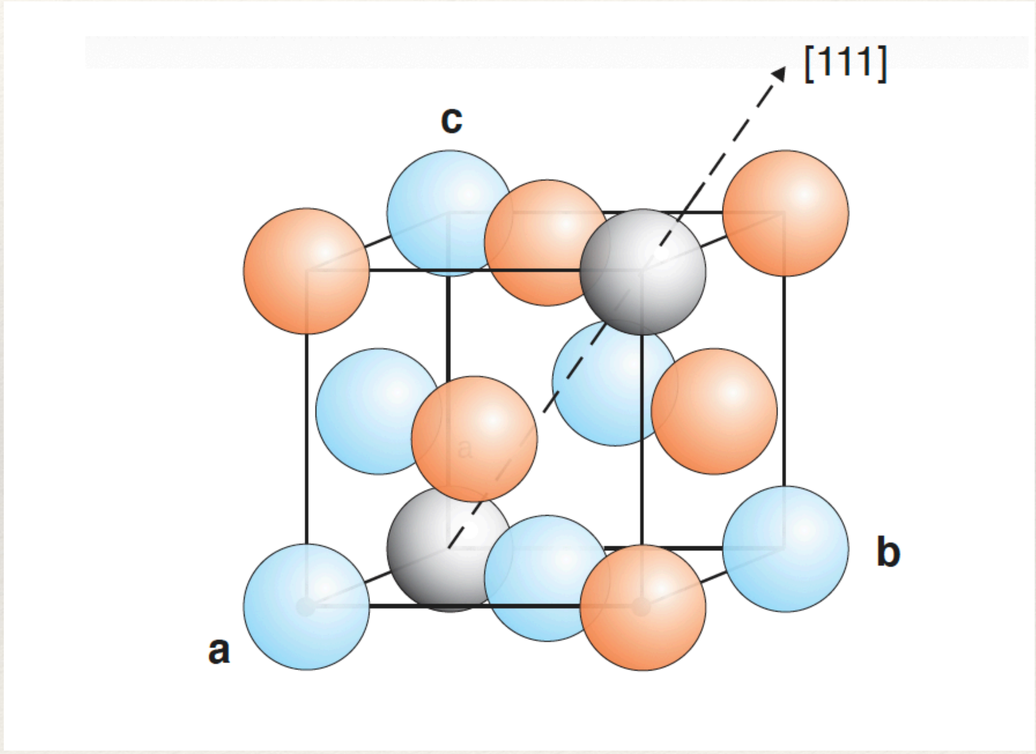


Close packing of hard spheres

Cubic close-packing

The minimal unit cell required to describe this structure is cubic!





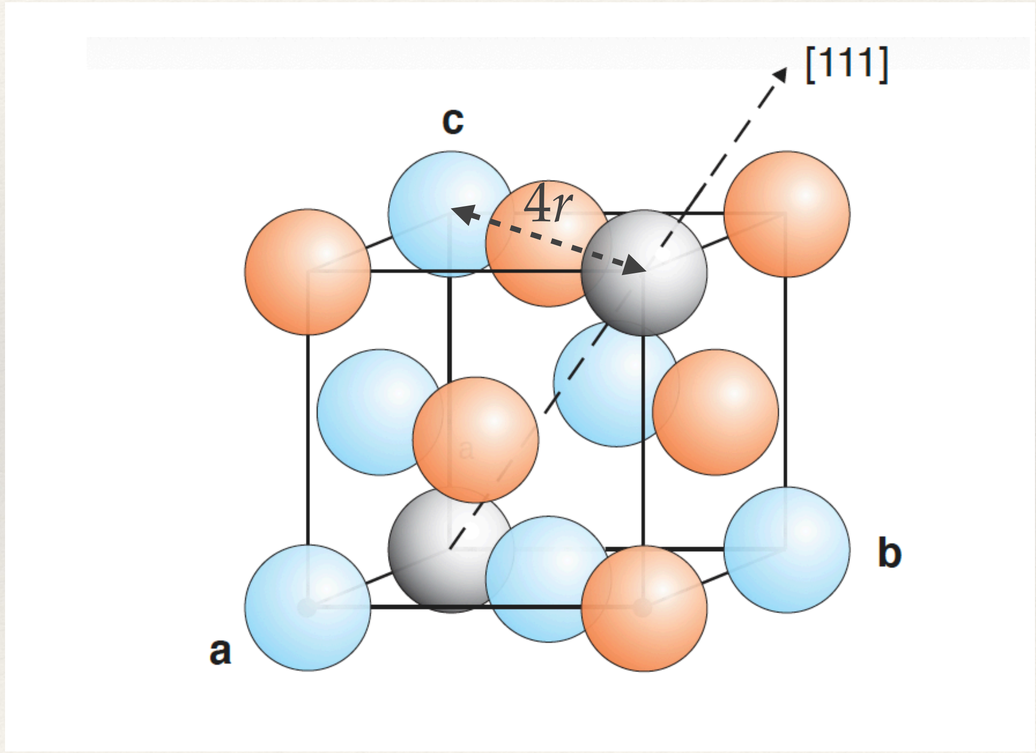
Same as the *A1* structure

Close packing of hard spheres

Cubic close-packing

If the spheres just touch then the relation between sphere radius r and the lattice parameter a is

$$r = \frac{a}{\sqrt{8}}$$



Spacing between adjacent planes is

$$d = \sqrt{3}a/3 \approx 1.633r$$

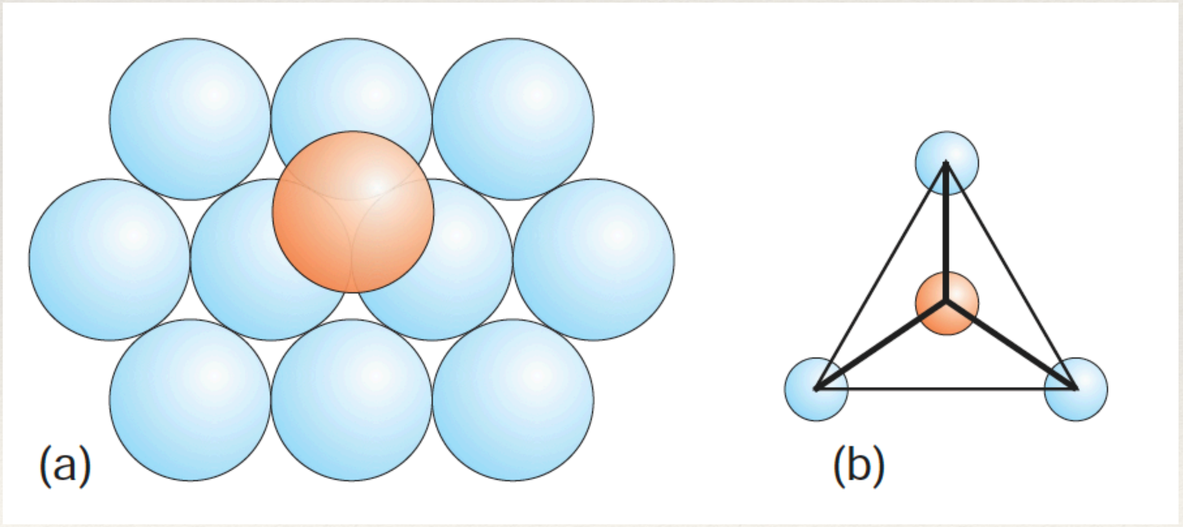
which is identical to the hcp structure.

Ideal packing fraction in both hcp and ccp is 0.7405. (Calculate as H.W.)

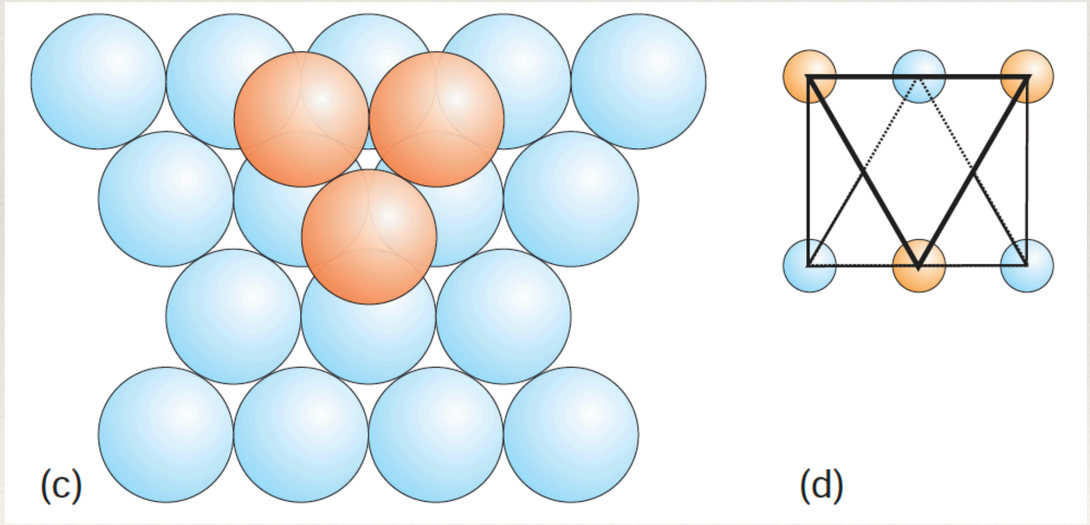
Close packing of hard spheres

Voids in the close-packed structure

Ionic crystals can be often described in terms of close-packing of anions. Cations then occupy voids that occur in the layers.



Tetrahedral Void



Octahedral Void

Close packing of hard spheres

Voids in the close-packed structure

Both ccp and hcp structures have $2N$ tetrahedral voids and N octahedral voids for every N anions in the structure.

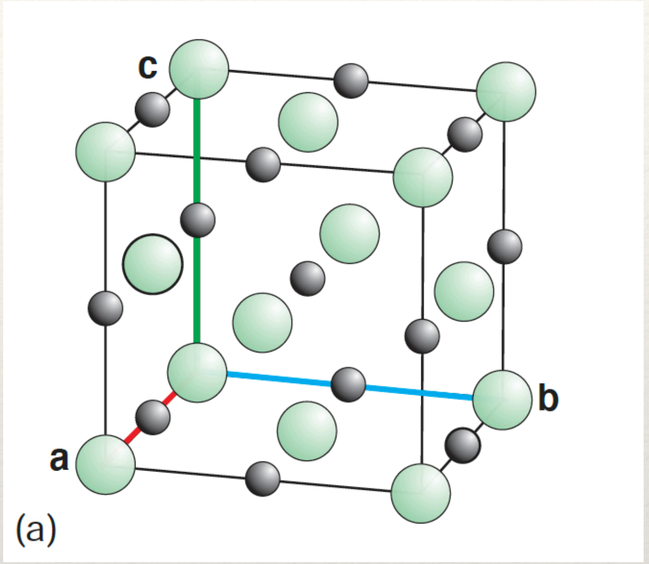
Cations are distributed in the available voids ensuring charge balance.

Formula for the structure can be found by counting the numbers of ion of each kind present.

Close packing of hard spheres

Examples

Halite could be considered a ccp structure formed by X ions and the M ions occupying all available octahedral voids.



=> formula is MX

Note that the charge on M and X must be equal in magnitude and opposite in sign.

In the nicolite structure (NiAs) the anions adopt a hcp structure with all octahedral voids filled with cations. E.g., NiAs, CoS, VS, FeSe and TiS.

Close packing of hard spheres

Examples

Spinel (*H1*) structure - AB_2X_4

X anions form ccp structure.

A cations occupy 1/8th of the tetrahedral voids

B cations occupy 1/2 of the octahedral voids

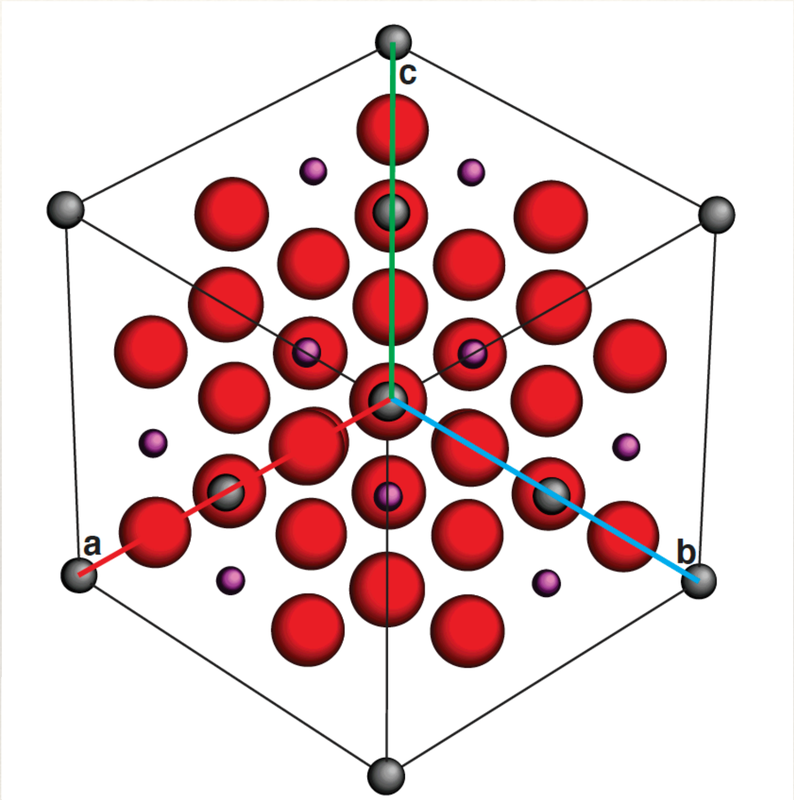
Ex., $MgAl_2O_4$

The unit cell is 2x2x2 of the standard cubic cell

=> 32 O^{2-} ions, 32 Oh voids and 64 Td voids

=> 8 Mg^{2+} ions and 16 Al^{3+} ions

Total charge = 32 x (-2) + 8 x (2) + 16 x (3) = 0



Close packing of hard spheres

Examples

Inverse Spinel structure - $(B)[AB]X_4$

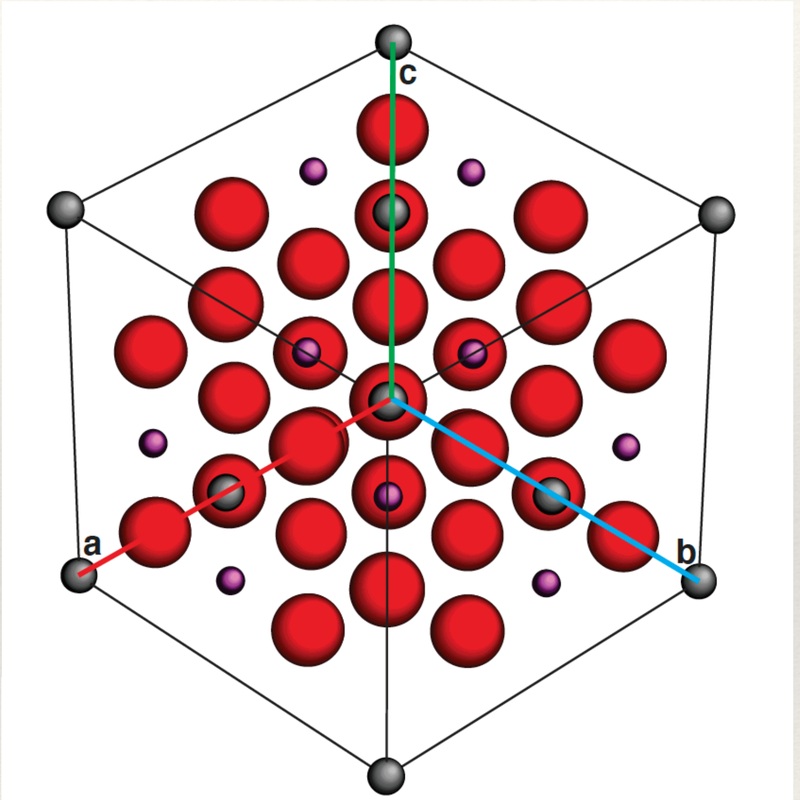
X anions form ccp structure.

A cations occupy 1/2 of the octahedral voids

B cations occupy 1/2 of the octahedral voids plus $1/8^{th}$ of the tetrahedral voids

Ex., Fe_3O_4 or $(Fe^{2+})[Fe^{2+}Fe^{3+}]O_4$

Is it charge neutral?

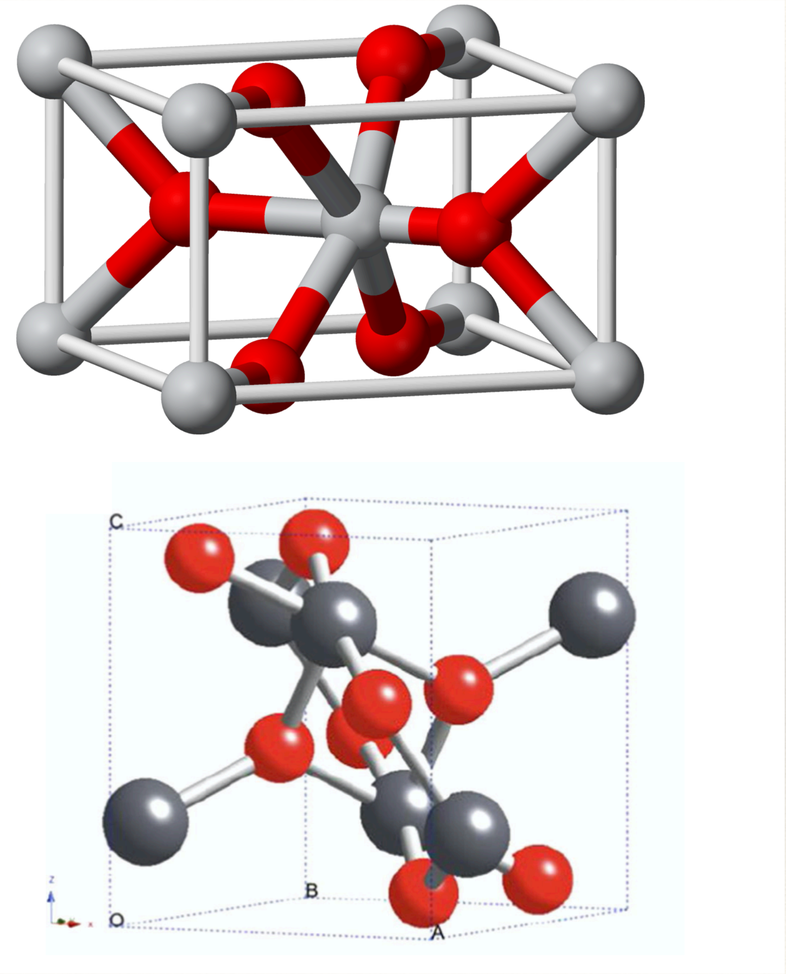


Close packing of hard spheres

Examples
Rutile - MX_2

X anions form hcp structure.
M cations occupy 1/2 of the Oh voids

Ex., TiO_2 and α-PbO_2



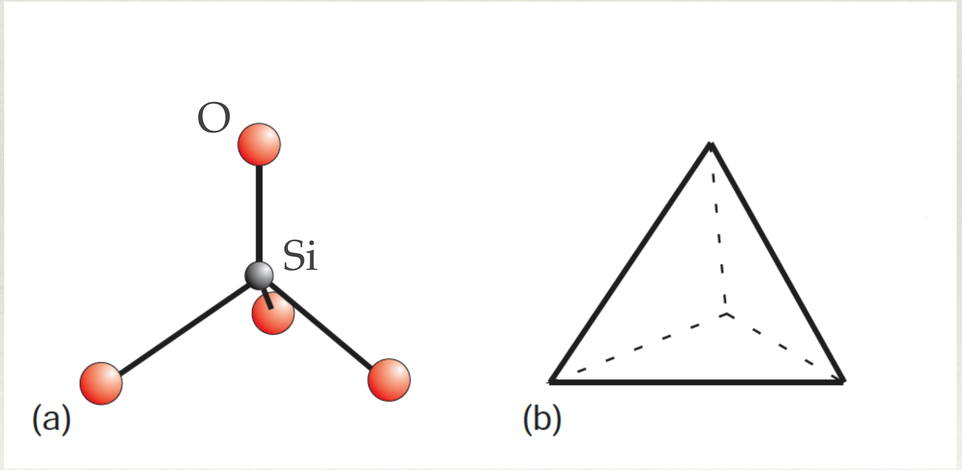
doi.org/10.1016/j.optmat.2016.02.031

Polyhedral Representation

In compound crystals it is often useful to view the building units as a particular atom/ion surrounded by a polydehron of the nearest neighbour atoms.

The vertices of the polyhedra are usually anions/non-metals and the centre is cation/metal.

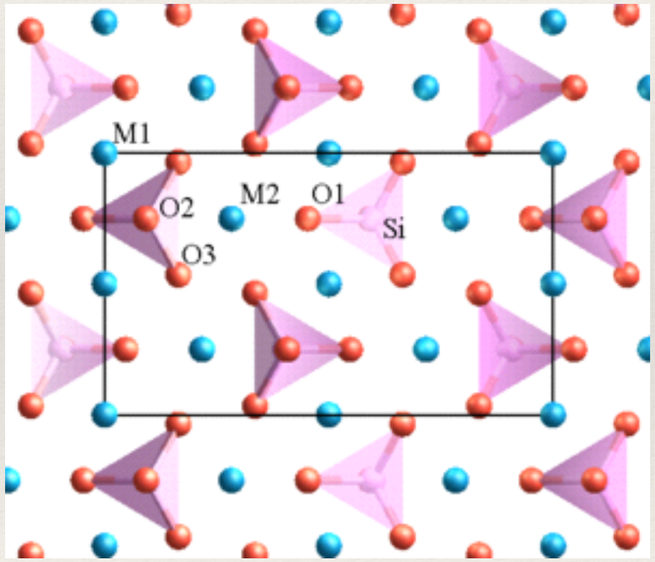
An illustrative example of this is SiO_2 which is made up of linked $[SiO_4]$ units.



Polyhedral Representation

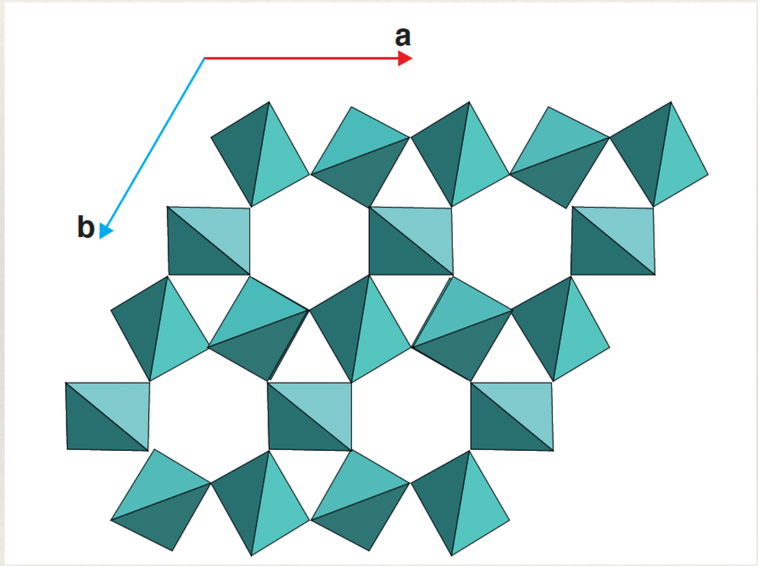
Examples Silicates

Independent tetrahedra



M_2SiO_4 (olivine)

Corner-sharing tetrahedra

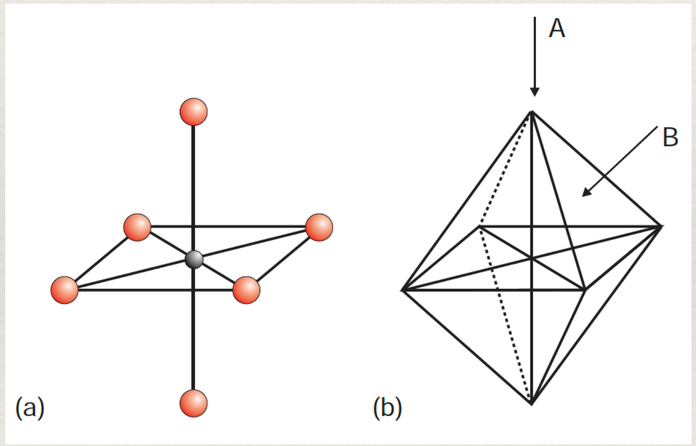


β-quartz

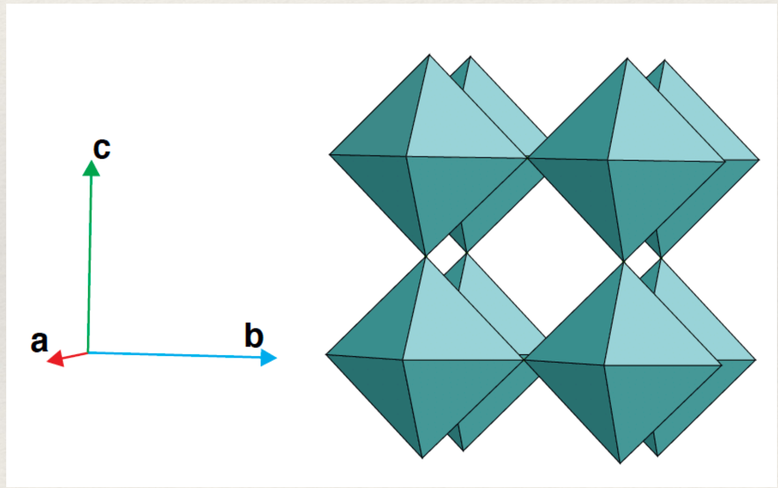
Polyhedral Representation

Examples

Anion octahedra around TM ion



Corner-sharing Octahedra



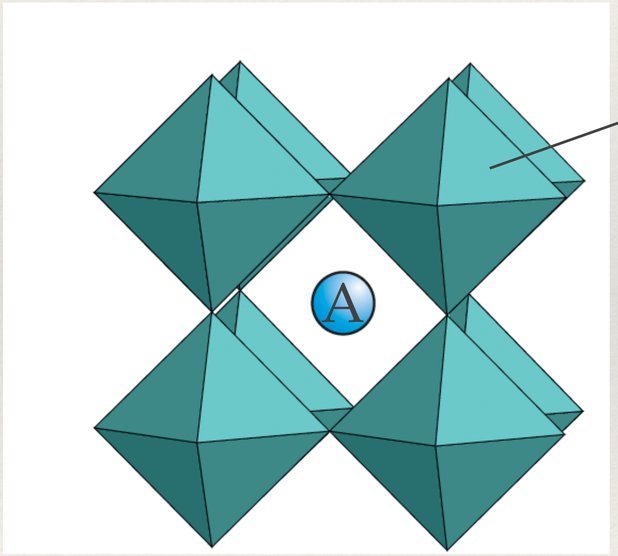
ReO_3 (cubic)

WO_3 (monoclinic with distorded Oh)

Polyhedral Representation

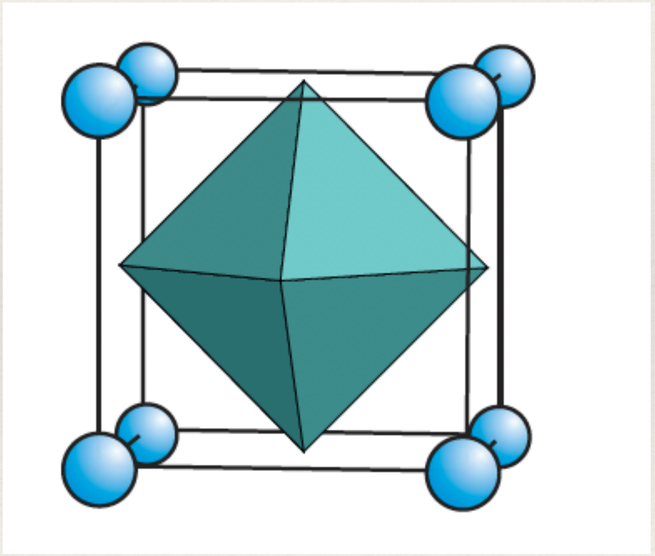
Perovskite structure (ABO_3)

A-centred unit cell



BO_6
Octahedra

B-centred unit cell



Examples - $PbTiO_3$, $BaTiO_3$, $BiFeO_3$, $CsPbBr_3$

We will spend some more time with perovskites later on