X-ray Diffraction

Principle

x-ray

X-ray scattered by electrons

Crystal planes
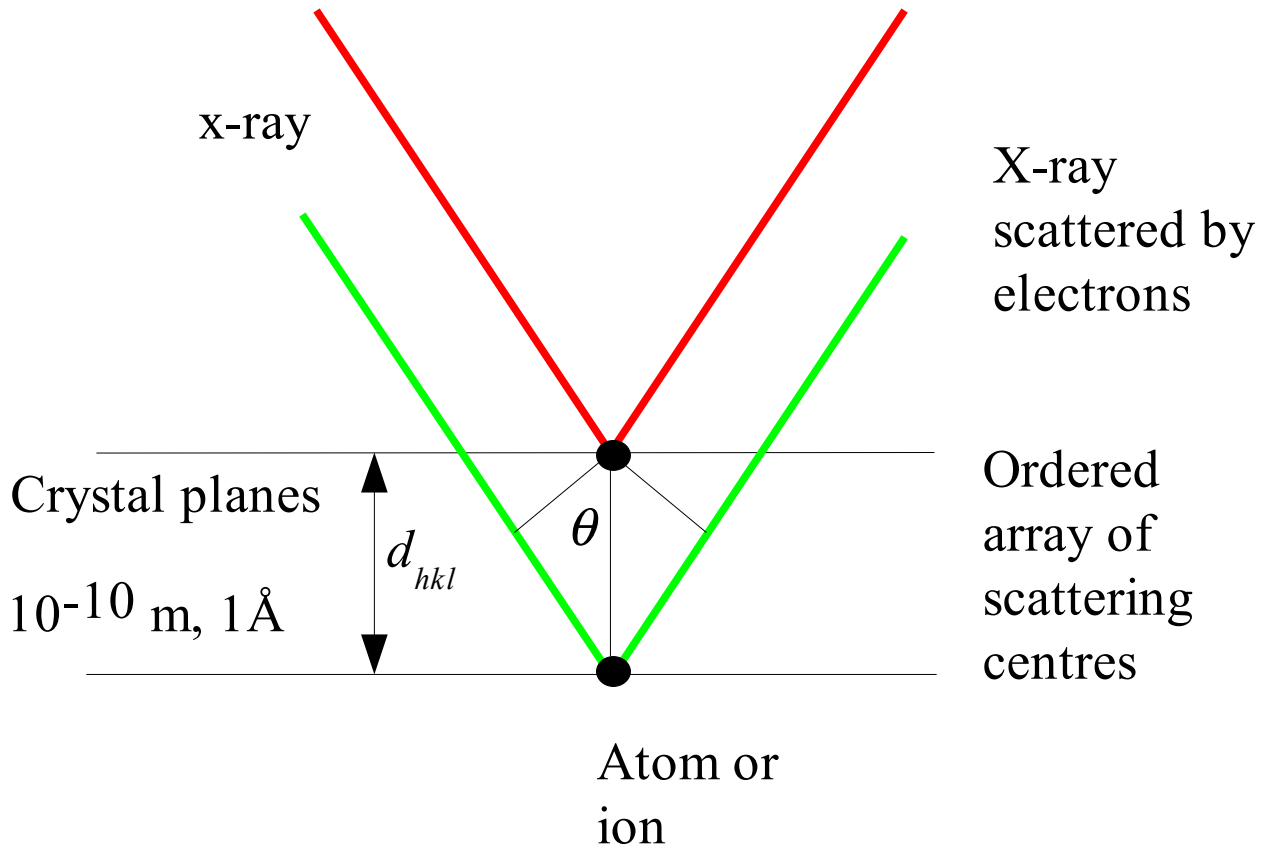
d_{hkl}

θ

10^{-10} m, 1Å

Ordered array of scattering centres

Atom or ion

Bragg equation
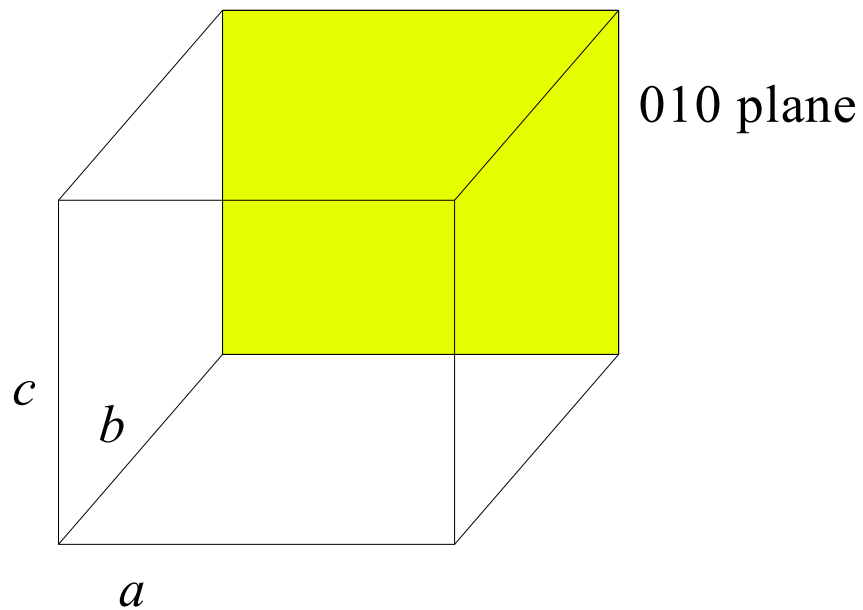 Condition for diffracted beams to be in phase

$$2d_{hkl}\sin \theta = n\lambda$$

Need to relate d_{hkl} to the unit cell dimensions

hkl = Miller indices

Define a plane which intercepts the unit cell at
a/h, b/k and c/l along a,b and c respectively

If zero plane lies parallel to this axis

010 plane

c b a

Parallel to a , $h = 0$
Intercepts b at b, $k = 1$
Parallel to c, $l = 0$

For a cubic system

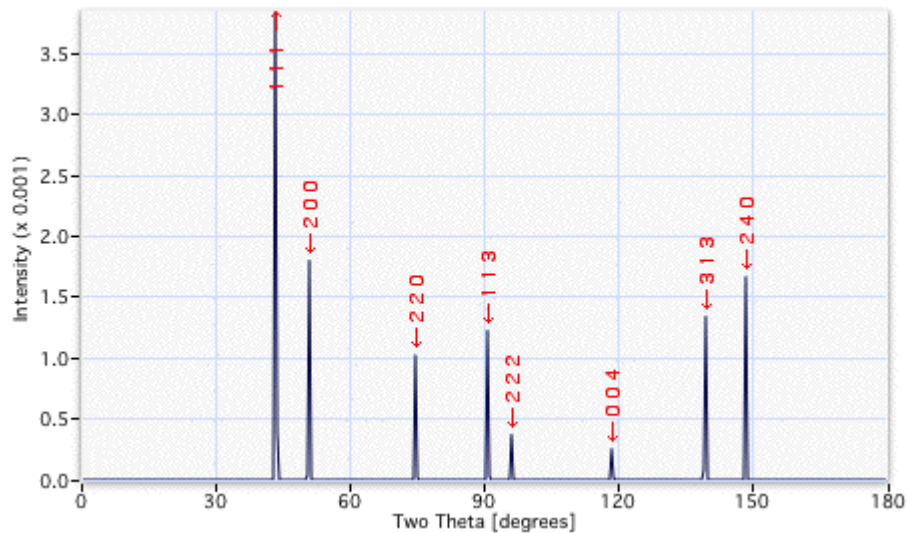$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \quad \text{with} \quad n\lambda = 2d\sin\theta$$

so

$$\frac{1}{d} = 2\sin\frac{\theta}{\lambda}$$

$$\frac{1}{d^2} = \frac{4\sin^2\theta}{\lambda^2}$$

$$\sin^2\theta = \frac{\lambda^2}{4a^2}\left(h^2 + k^2 + l^2\right)$$

Powder diffraction

Experimental data

(H. K. D. H. Bhadeshia Ni-Ti-Al alloy, F-cubic

http://www.msm.cam.ac.uk/phase-trans/2003/Superalloys/superalloys.html)

Factors affecting the intensity and number of peaks

1. Crystal class
2. Lattice type
3. Symmetry
4. Unit cell parameters
5. Distribution/type of atoms in the unit cell

Uses of powder x-ray diffraction data

A. Identification of unknown materials

JCPDS (Joint Committee on Powder Diffraction Standards) Database
  150,000 unique powder diffraction data sets

B. Phase purity

Follow reactions, monitor purity of samples

But care required with quantification
  - diffracted intensity depends on the number of
    electrons so greater for heavy atoms

  - amorphous materials will not give diffraction peaks

C. Lattice parameters

First must index the diffraction pattern

Indexing

Assign Miller indices to a reflection in the diffraction pattern.

Complication

       not all reflections are seen because of destructive interference between diffracted waves

       depends on lattice type

       systematic absences

Example

Primitive cubic cell

All reflections allowed, all combinations of h,k and l allowed

Experimental data is 2θ

          this gives θ

Equation has $\sin^2\theta$, draw up Table

$$\sin^2\theta = \frac{\lambda^2}{4a^2}(h^2 + k^2 + l^2)$$

2θ	$\sin^2\theta$	Ratio	
19.213	0.0279	1	
27.302	0.0557		
33.602	0.0836		
38.995	0.1114		

Smallest 2θ occurs when $h = 1$, $k = 0$, $l = 0$

So guess 19.213 is (100) and look at ratio of $\sin^2\theta$
Since

$$\text{Ratio} = \frac{(h_1^2 + k_1^2 + l_1^2)}{(h_2^2 + k_2^2 + l_2^2)}$$

Expect ratio to be just $\quad (h_1^2 + k_1^2 + l_1^2)$

2θ	$\sin^2\theta$	Ratio	Miller indices
19.213	0.0279	1	100
27.302	0.0557	2	110
33.602	0.0836	3	111
38.995	0.1114	4	200

What if the lowest observed reflection is not (100)?

This is equivalent to not observing the 19.213

Still start by assuming first observed reflection is (100)

2θ	$\sin^2\theta$	Ratio	Miller indices
27.302	0.0557	1	
33.602	0.0836	1.5	
38.995	0.1114		

Ratio is not an integer value, so therefore cannot be (100)

Now try the next lowest (110)

$$\left(h_1^2 + k_1^2 + l_1^2\right) = 2$$

Base $\sin^2\theta$ for ratio must be 0.0557/2 = 0.0279

Use this value to find all the ratios

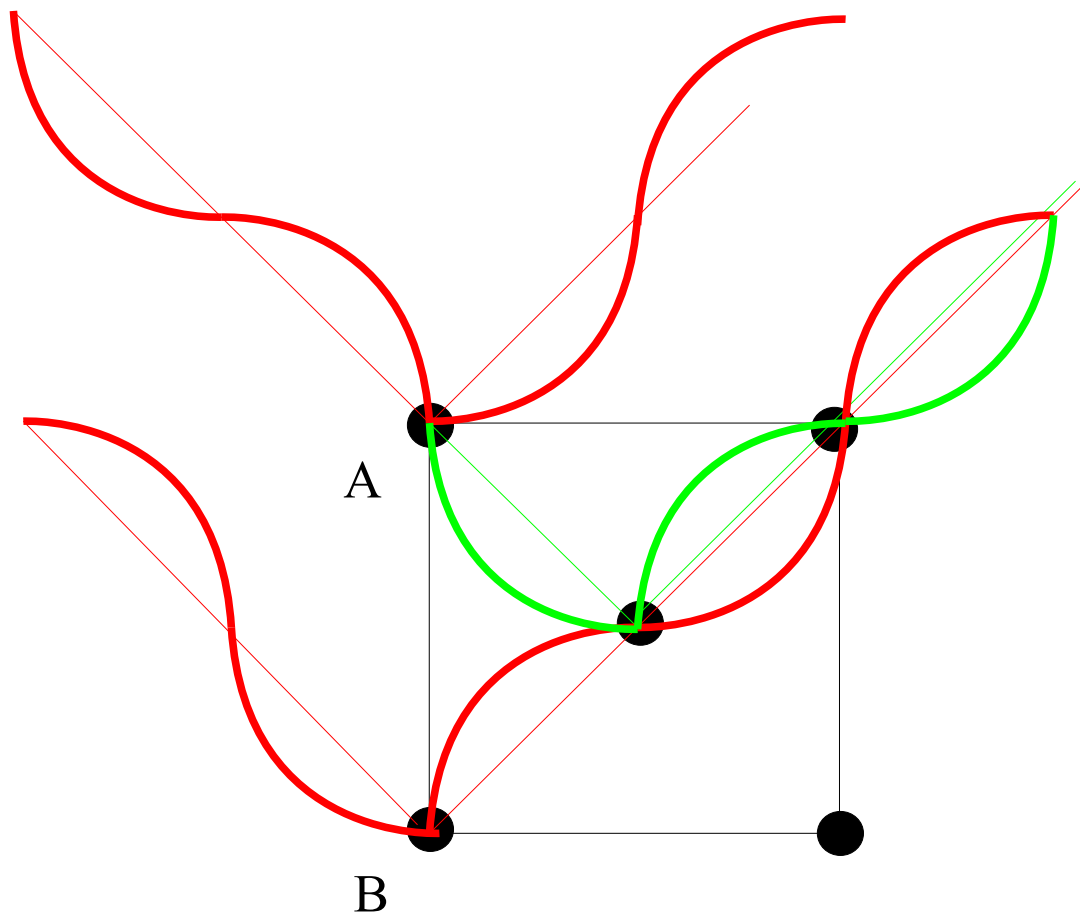| 2θ	$\sin^2\theta$	Ratio	Miller indices
27.302	0.0557	2	110
33.602	0.0836	3	111
38.995	0.1114	4	200

Integer ratios again.

Lattice type and Systematic absences

Absent reflections depending on the lattice type

Destructive interference between diffracted waves

100 plane in body centred cubic

A and B always in phase,
Diffraction from atom at body centre always ½ λ out of phase

Total destructive interference of 100 reflection

General condition for body centred cubic

$$h+k+l=2\mathrm{n}$$

Can lead to problems in indexing because the lowest reflection will be (110)

Index

2θ	$\sin^2\theta$	Ratio	x 2
10.97	0.0091	1	2
15.54	0.0182	2	4
19.06	0.0274	3	6
22.05	0.0366	4	8
24.69	0.0457	5	10
27.09	0.0549	6	12
29.30	0.0640	7	14
31.38	0.0730	8	16

But cannot get 7 from $(h^2+k^2+l^2)$

First reflection cannot be (100) must be (110)

Base $\sin^2\theta$ for ratio must be 0.0091/2 = 0.00455 and lattice type must be body centred cubic

Perovskite

Primitive cubic with X (B) at the lattice points
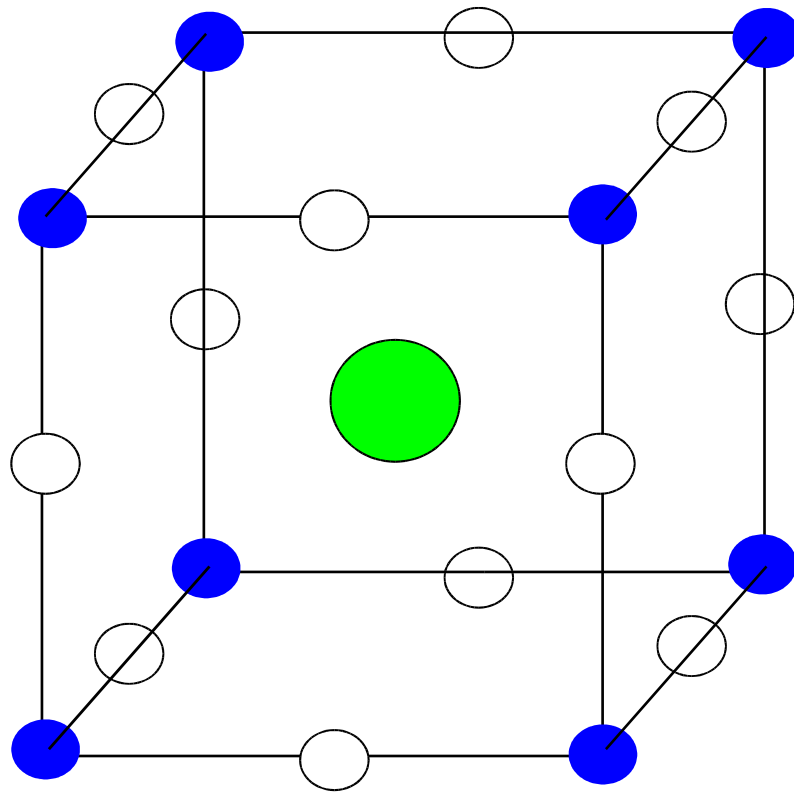

● B
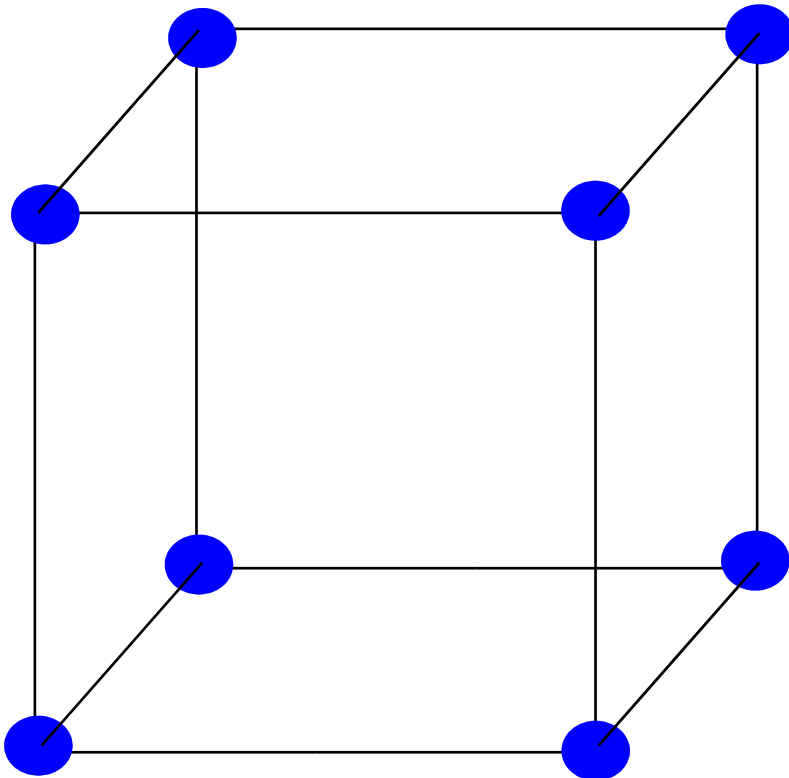
Place O (Y) atom halfway along each edge

B

O
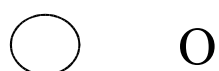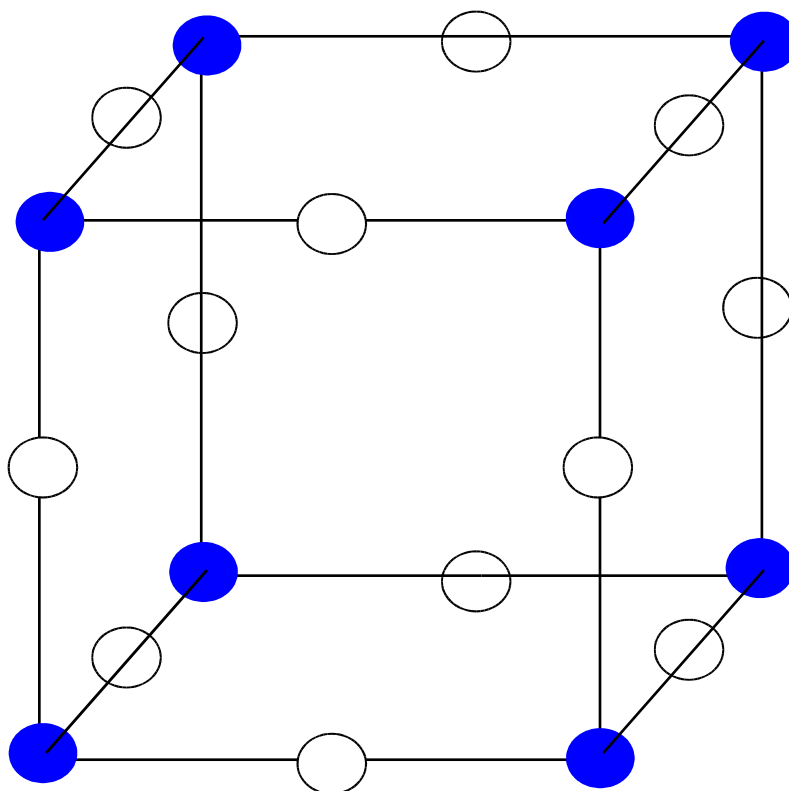
What is the geometry around B?

What is the overall formula?

ReO₃
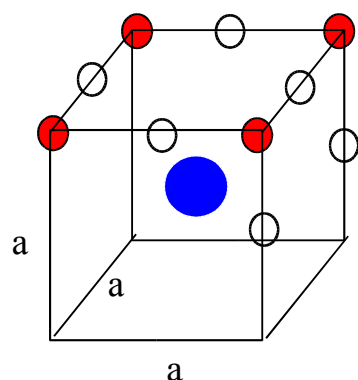
Place an atom A at the body centre of the cube
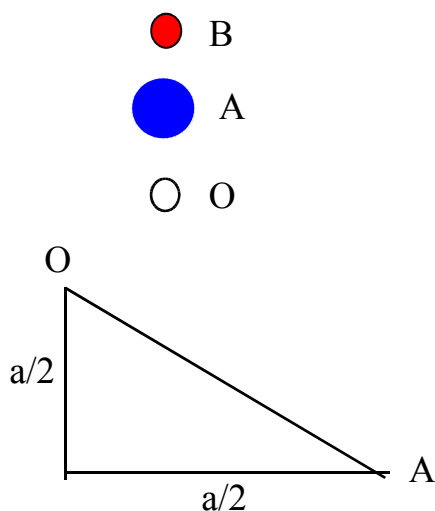
B

O

A

Coordination of the atom at the centre?
Size of A? Which elements?
What is the general formula?

Radius ratio rules

r_A = ionic radius of A
r_B = ionic radius of B
r_O = ionic radius of oxygen

$$a = 2(B\text{-}O) = 2(r_B + r_O)$$

$$(A\text{-}O) = ([a/2]^2 + [a/2]^2)^{1/2} = (a^2/2)^{1/2}$$
$$= a/\sqrt{2} = (r_A + r_O)$$

$$a = \sqrt{2}(r_A + r_O) = 2(r_B + r_O)$$

This condition must be satisfied for a perfect fit. In practise no fits are perfect hence we introduce a tolerance factor, t. t is 1.000 for a perfect fit

$$\sqrt{2}(r_A + r_O) = 2t(r_B + r_O)$$

For SrTiO$_3$ we have: rSr^{2+} = 1.58 A
rTi^{4+} = 0.745 A
rO^{2-} = 1.26 A

$t = \sqrt{2}(1.58 + 1.26)/2(0.745 + 1.26) = 1.002.$

Values between 0.9 and 1.0 are seen for an ideal cubic structure.

Distorted pervoskite t = 0.85-0.9 and 1.0-1.06
Either A is too small and rattles around in the hole or A is too large and forces the structure apart.

For example $BaTiO_3$ t=1.06
The barium atoms are too large expanding the lattice. This in turn means the Ti is in a larger cavity than it would prefer so a distortion takes place allowing some shorter Ti-O distances.
Tetragonal distortion a=b≠c.
Ba^{2+} is also displaced slightly in the same direction. This means that the 'centres of gravity' of the positive and negative charges within the cell no longer coincide generating a dipole - basis for ferroelectricity. Consider this in more detail later.

Cuprate superconductors

Major advance in mid 1980's

$YBa_2Cu_3O_{7-\delta}$ $0 < \delta < 1$ for δ close to zero $T_c = 93$ K $>$ liq N_2.

Take three perovskite cells
(with Cu as lattice point B)

Y

B
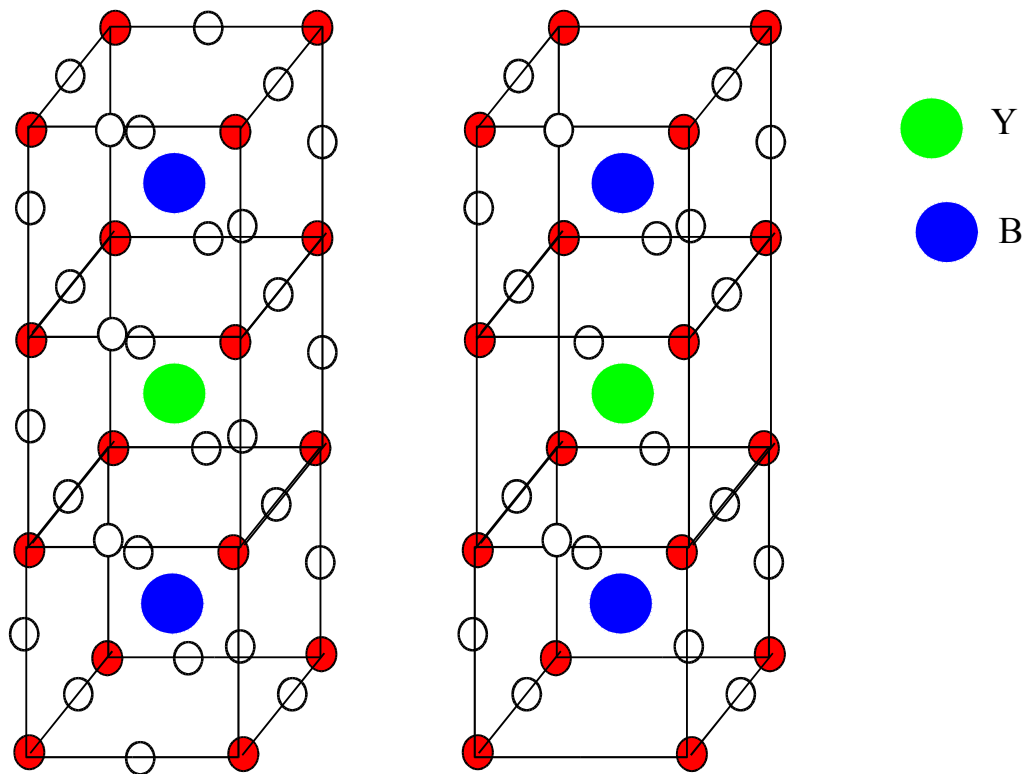
Remove O from plane around Y and 1/2 O from top and bottom faces.
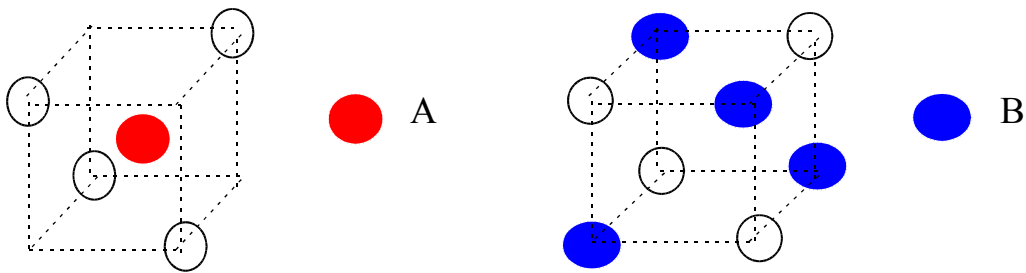
How many different Cu environments?

Spinel structure

Archetypal compound $MgAl_2O_4$ -
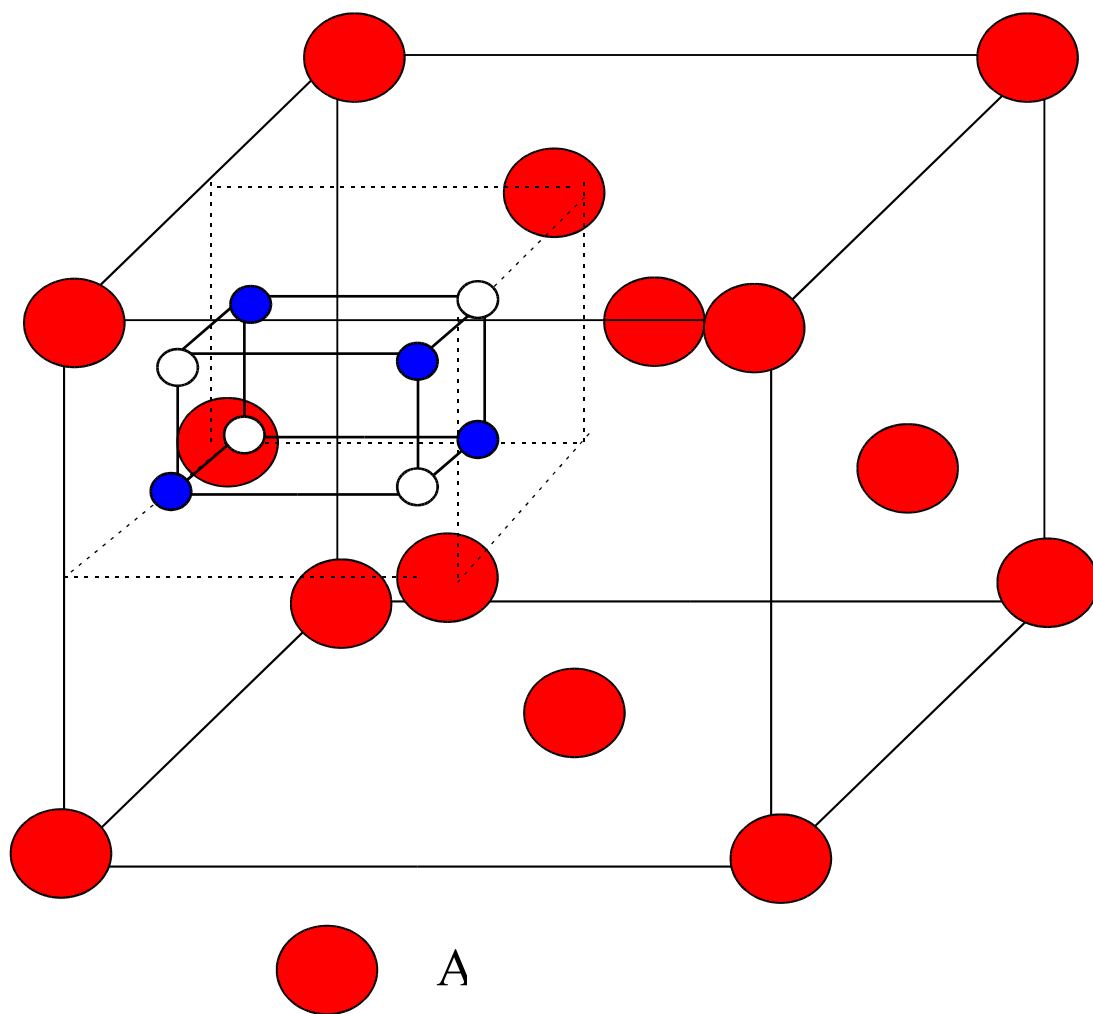
shows stoichiometry - AB_2X_4

A and B are about the same size and X is commonly O or S

Imagine there are eight smaller cube: Either A of B type

These eight octants consist of alternating AO_4 tetrahedra and B_4O_4 cubes.

Place these within an encompassing fcc lattice of A atoms

A

Stoichiometry:

F centred A	= 1/8 x 8 + 1/2x 6 = 4A
4 x AO_4 tetrahedra	= 4A + 16O
4 x B_4O_4 cubes	= 16B + 16O
	$A_8B_{16}O_{32}$ = AB_2O_4