

# Lecture 1 - Ionic structures

# Lecture Summary

- Types and applications of ionic materials
- Crystallography recap
- Lattice energy and ionic bonding
- Close-packing and ionic structure types

# Introduction

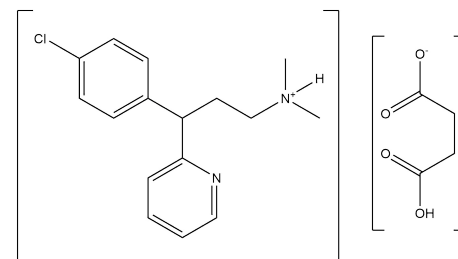
'Ionic materials' consist of both cations and anions:

- Many inorganic solids
  - e.g.  $\text{Na}^+\text{Cl}^-$  and  $\text{Mg}^{2+}\text{SO}_4^{2-}$

# Introduction

'Ionic materials' consist of both cations and anions:

- Many inorganic solids
  - e.g.  $\text{Na}^+ \text{Cl}^-$  and  $\text{Mg}^{2+} \text{SO}_4^{2-}$
- Organic salts
  - ammonium acetate  $\text{NH}_4^+ \text{CH}_3 \text{COO}^-$
  - chlorphenirammonium maleate  
(active part of Piriton®)

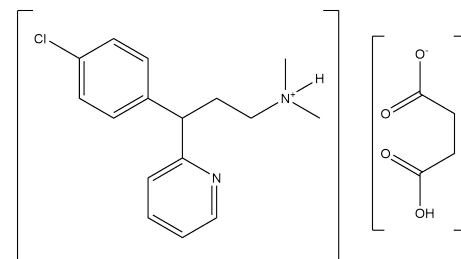


Chlorphenirammonium maleate

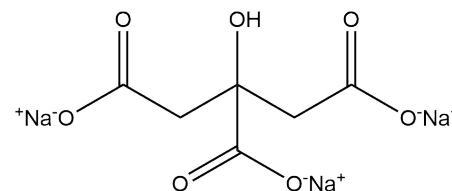
# Introduction

'Ionic materials' consist of both cations and anions:

- Many inorganic solids
  - e.g.  $\text{Na}^+ \text{Cl}^-$  and  $\text{Mg}^{2+} \text{SO}_4^{2-}$
- Organic salts
  - ammonium acetate  $\text{NH}_4^+ \text{CH}_3 \text{COO}^-$
  - [chlorpheniraminium maleate](#)  
(active part of Piriton®)
- (in)organic salts
  - Mono-/Di-/Tri-Sodium citrate  
 $\text{Na}_x \text{C}_6 \text{H}_{8-x} \text{O}_7$ 
    - collectively used as E331 in food
    - x can be varied from 1–3



Chlorpheniraminium maleate

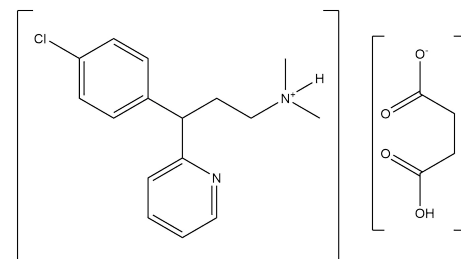


Trisodium Citrate (x=3)

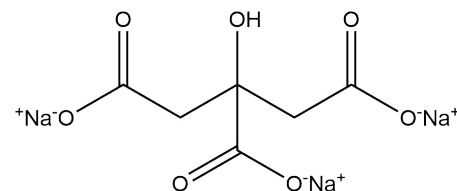
# Introduction

'Ionic materials' consist of both cations and anions:

- Many inorganic solids
  - e.g.  $\text{Na}^+ \text{Cl}^-$  and  $\text{Mg}^{2+} \text{SO}_4^{2-}$
- Organic salts
  - ammonium acetate  $\text{NH}_4^+ \text{CH}_3 \text{COO}^-$
  - [chlorpheniraminium maleate](#)  
(active part of Piriton®)
- (in)organic salts
  - Mono-/Di-/Tri-Sodium citrate  
 $\text{Na}_x \text{C}_6 \text{H}_{8-x} \text{O}_7$ 
    - collectively used as E331 in food
    - x can be varied from 1–3
- Ionic liquids
  - Either organic or inorganic, liquid below 100 °C



Chlorpheniraminium maleate



Trisodium Citrate (x=3)

# Why are they interesting?

- Large range of practical applications
  - important for energy storage, but lots of other applications!
  - ionic liquids are gaining attention for many applications

# Why are they interesting?

- Large range of practical applications
  - important for energy storage, but lots of other applications!
  - ionic liquids are gaining attention for many applications
- High melting points due to Coloumbic energy (see [later](#))



# Why are they interesting?

- Large range of practical applications
  - important for energy storage, but lots of other applications!
  - ionic liquids are gaining attention for many applications
- High melting points due to Coloumbic energy (see [later](#))
- Electrically insulating
  - Electronegativity differences promote localised electrons



# Why are they interesting?

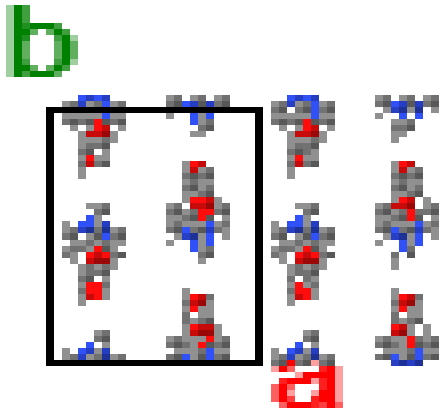
- Large range of practical applications
  - important for energy storage, but lots of other applications!
  - ionic liquids are gaining attention for many applications
- High melting points due to Coloumbic energy (see [later](#))
- Electrically insulating
  - Electronegativity differences promote localised electrons
- Usually hard, and often robust to harsh conditions
  - e.g. Synroc is used to encapsulate nuclear waste



# We can divide solids into two categories:

## Molecular (e.g. paracetamol)

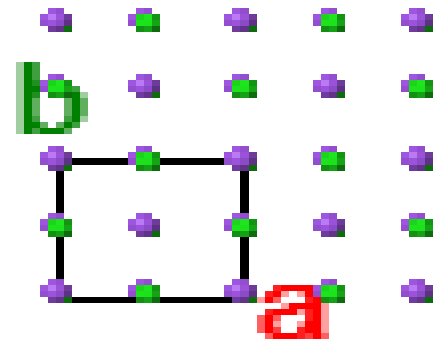
- Strong intramolecular bonds
- Weaker intermolecular interactions



JSmol

## Infinite (e.g. NaCl)

- Strong bonds between all atoms
- No discrete molecules

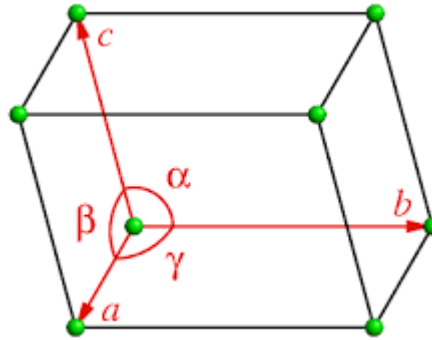


JSmol

We'll concentrate on **infinite materials**.

# Recap on crystal structure

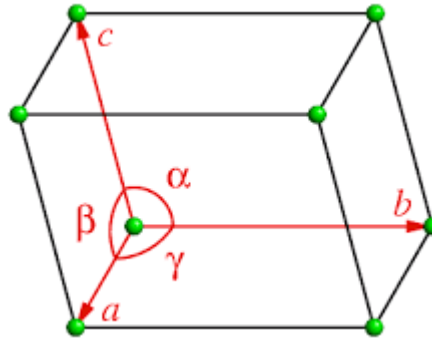
Periodic solids can be described by a unit cell



- Defined by lengths ( $a$ ,  $b$ ,  $c$ ) and angles ( $\alpha$ ,  $\beta$ ,  $\gamma$ )
  - 'Lattice parameters'

# Recap on crystal structure

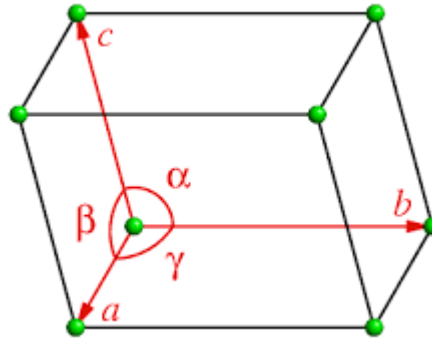
Periodic solids can be described by a unit cell



- Defined by lengths ( $a$ ,  $b$ ,  $c$ ) and angles ( $\alpha$ ,  $\beta$ ,  $\gamma$ )
  - 'Lattice parameters'
- Possesses 'space group' symmetry (an extension to point groups)

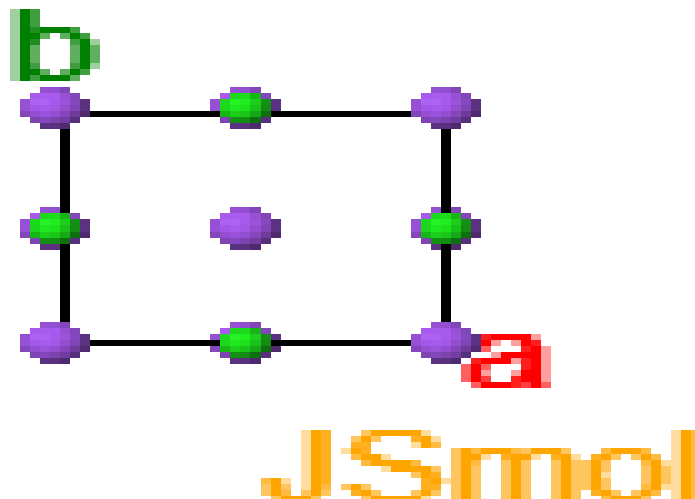
# Recap on crystal structure

Periodic solids can be described by a unit cell



- Defined by lengths ( $a$ ,  $b$ ,  $c$ ) and angles ( $\alpha$ ,  $\beta$ ,  $\gamma$ )
  - 'Lattice parameters'
- Possesses 'space group' symmetry (an extension to point groups)
- Atom positions defined by fractional position along lattice directions

# Example: Sodium chloride



Cubic structure	$a = b = c = 5.62 \text{ \AA}, \alpha = \beta = \gamma = 90^\circ$		
Spacegroup	$Fm\bar{3}m$ (#225, point group = $O_h$ )		
Na atoms at:	$(0\ 0\ 0)$ $\frac{1}{2}$	$(\frac{1}{2}\ \frac{1}{2}\ 0)$	$(\frac{1}{2}\ 0\ \frac{1}{2})$ $(0\ \frac{1}{2}\ \frac{1}{2})$ (all symmetry-related)
Cl atoms at:	$(\frac{1}{2}\ 0\ 0)$ $\frac{1}{2}$	$(0\ \frac{1}{2}\ 0)$	$(0\ 0\ \frac{1}{2})$ $(\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2})$ (all symmetry-related)

# Ionic Bonding

- Ionic compounds stay together because of electrostatic interactions (strong)



# Ionic Bonding

- Ionic compounds stay together because of electrostatic interactions (strong)
- Total electrostatic energy is the (infinite) sum over *all* ion pairs,

$$E_{\text{Madelung}} = \sum_{i \neq j} \frac{q_i q_j}{4\pi\epsilon_0 r}$$

$q$  is the charge on ions  $i$ ,  $j$  and  $r$  is the distance between them

# Ionic Bonding

- Ionic compounds stay together because of electrostatic interactions (strong)
- Total electrostatic energy is the (infinite) sum over *all* ion pairs,

$$E_{\text{Madelung}} = \sum_{i \neq j} \frac{q_i q_j}{4\pi\epsilon_0 r}$$

$q$  is the charge on ions  $i$ ,  $j$  and  $r$  is the distance between them

- $\frac{1}{r}$  dependence makes long-range interactions important

# Infinite summations

- For infinite solids, periodicity usually means the sum converges
  - As  $r$  increases, the contribution becomes smaller.

# Infinite summations

- For infinite solids, periodicity usually means the sum converges
  - As  $r$  increases, the contribution becomes smaller.
- An infinite sum can therefore be replaced by the Madelung constant
  - depends on the structure type

# Infinite summations

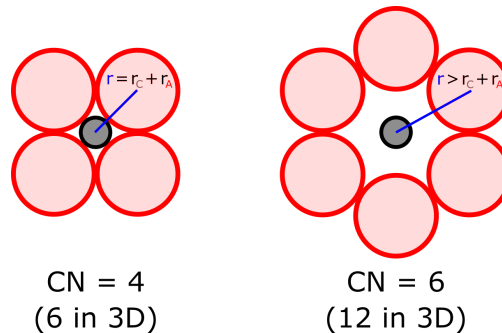
- For infinite solids, periodicity usually means the sum converges
  - As  $r$  increases, the contribution becomes smaller.
- An infinite sum can therefore be replaced by the Madelung constant
  - depends on the structure type
- e.g. for NaCl:

$$\begin{aligned} E_{\text{Madelung}} &= \sum_{i \neq j} \frac{q_i q_j}{4\pi\epsilon_0 r} \\ &= \frac{N_A q_i q_j}{4\pi\epsilon_0 r} \left( 6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{2} + \frac{24}{\sqrt{5}} - \dots \right) \\ &\simeq \frac{N_A q_i q_j}{4\pi\epsilon_0 r} \times 1.74756 \end{aligned}$$

# Ionic Structures

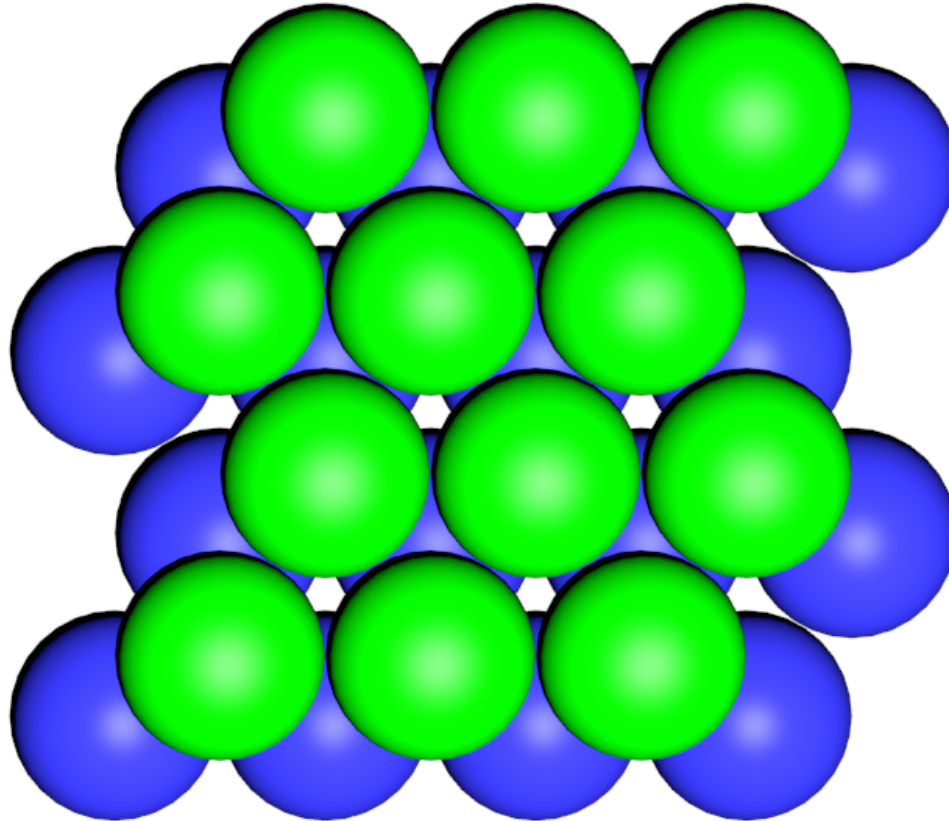
Generally, structures **maximise cation-anion** interactions (-ve energy) while **minimising like-charge** interactions (+ve energy)

- Maximise cation-anion coordination number
  - Ideally, ions should be densely packed



In many materials, the optimum is found when the largest ion (often oxide) is **close-packed**

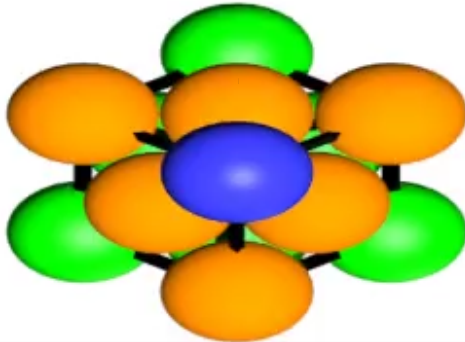
# Close packing



# Close packing

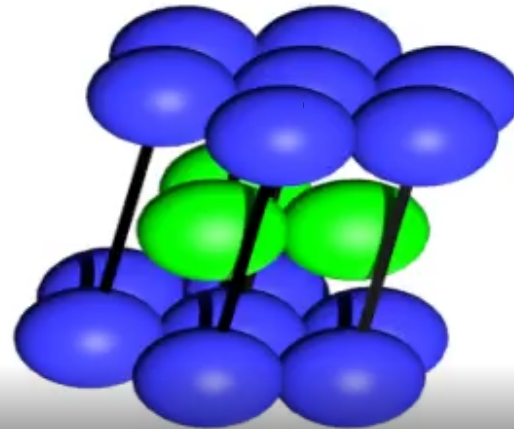
Face-centered cubic  
(FCC)

... ABCABC ...



Hexagonal close-packed  
(HCP)

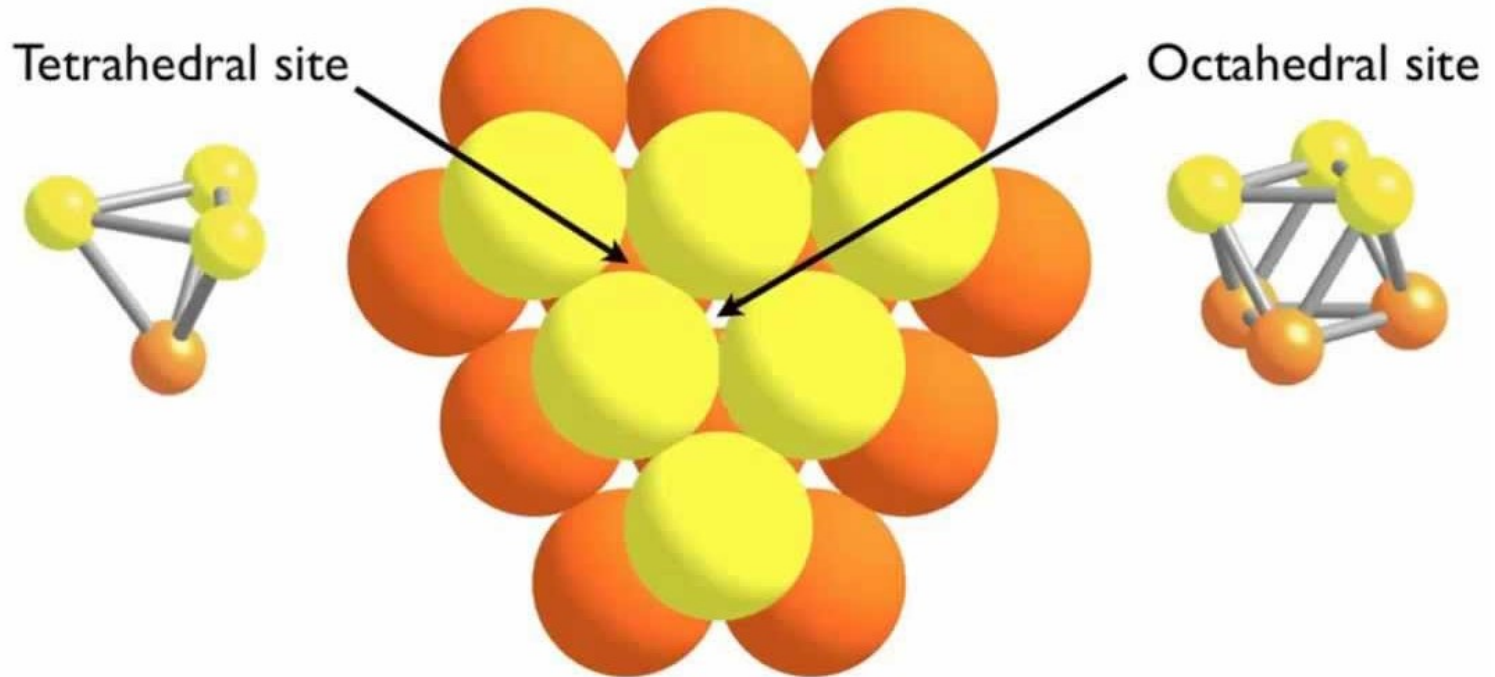
... ABABAB ...





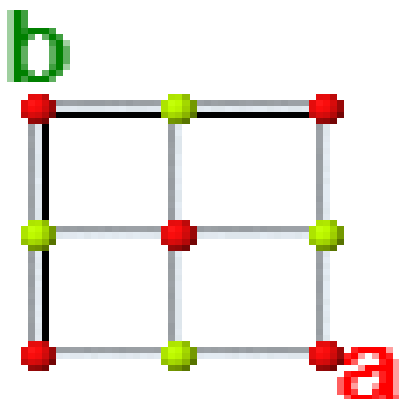
# Holes

CP arrangements of large (an)ions [X] leave 'holes' within the structure, which can be occupied by smaller (cat)ions [M]



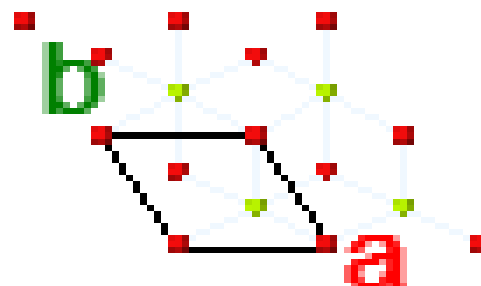
# Octahedral holes

One **hole** per **cp ion** - both are 6-coordinate



JSmol

Rock salt (NaCl) structure



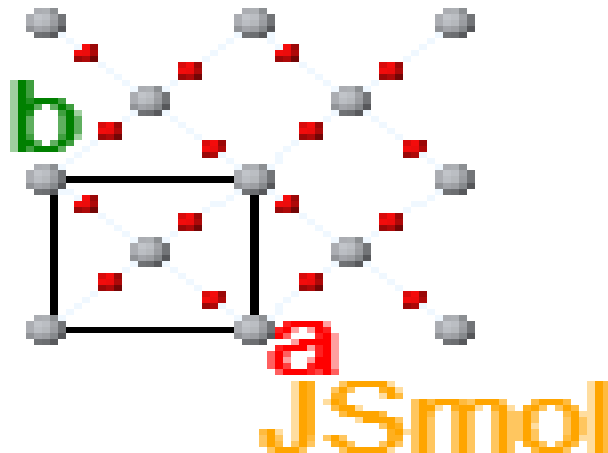
JSmol

Nickel Arsenide structure  
(e.g. FeS)



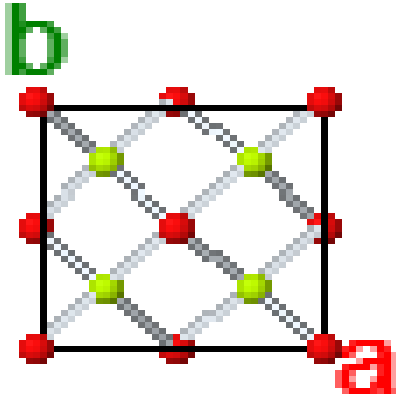
# Rutile

Although not strictly close-packed, rutile ( $\text{TiO}_2$ ) is distorted HCP with  $\text{Ti}^{4+}$  filling half the octahedral holes CN = 6 / 3

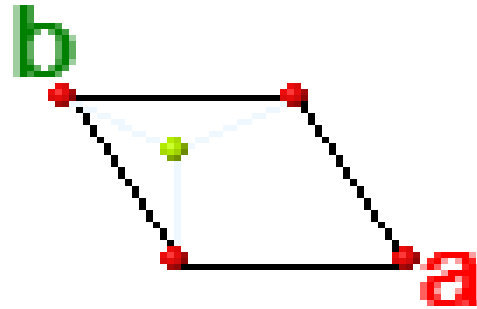


# Tetrahedral holes

Two holes per cp ion



JSmol



JSmol

Holes filled	FCC Type	CN(A/X)	HCP Type	CN(A/X)
All	Fluorite ( $\text{CaF}_2$ )	4/8	(not possible)	-
Half	Zinc-blende ( $\text{ZnS}$ )	4/4	Wurtzite ( $\text{ZnS}$ )	4/4

# Which structure type?

Generally, the structure formed depends on the ratio of ionic radii

- Smaller cations will prefer lower coordination numbers

$\frac{r^+}{r^-}$	Cation C.N.	MX Structure	MX <sub>2</sub> Structure
0.7 - 1.0	8	CsCl	CaF <sub>2</sub>
0.4 - 0.7	6	NaCl	TiO <sub>2</sub>
0.2 - 0.4	4	ZnS (Wurtzite/Zinc-blende)	Anti-fluorite (e.g. Li <sub>2</sub> S)

These are only approximate 'rules', and other binary structures exist (e.g. CdI<sub>2</sub>, CdCl<sub>2</sub>, PbO, etc...)

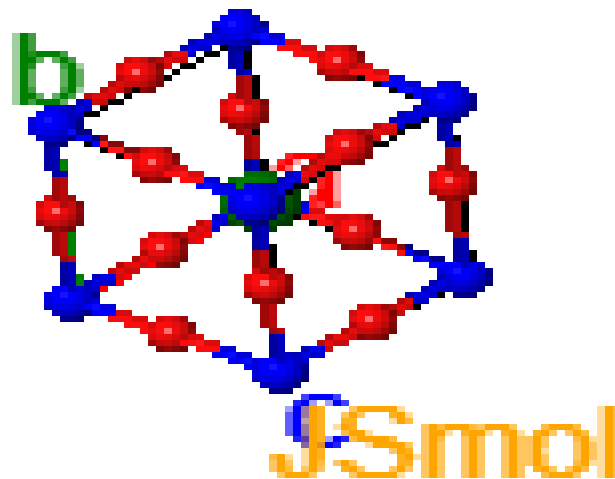
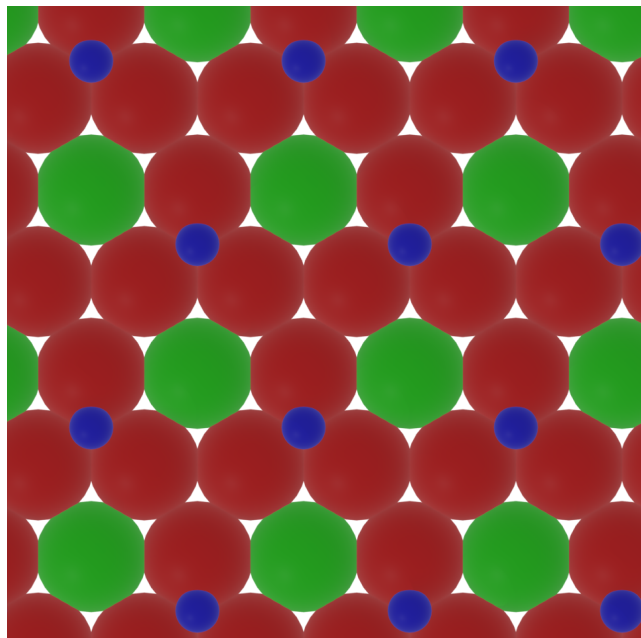
- Very difficult to predict!

# Beyond binary compounds

With 3 or more elements, structures become much more complicated!

An important one is perovskite,  $ABX_3$

- $r(A) \simeq r(X)$ , so can be considered as FCC  $AX_3$  layer with B filling 25% of octahedral holes:



# Lecture recap

- Variety of ionic materials with a range of applications
- Revision of basic crystallography
  - Unit cells, symmetry
- Electrostatic interaction hold ionic crystals together
  - Long-ranged
  - Aim to maximise cation-anion interactions
- Close-packing of anions often most stable
  - Ratio of ionic radii suggests which structure is adopted
  - Beyond binary compounds, predicting structures is hard!