

# Lecture 1 - Ionic structures

# Course Summary

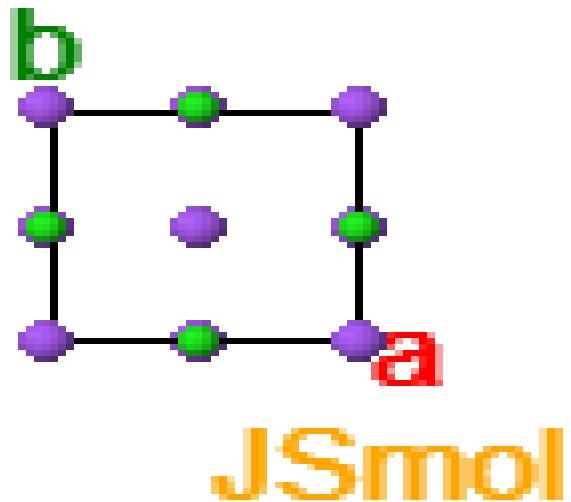
This course aims to introduce you to the importance of ionic materials in many applications.

What do I want you to do?

- Revise basic crystallography and ionic solids
- Try to understand examples, **don't memorise them**
- If in doubt - ask questions!

# Lecture Notes

- Interactive HTML notes
  - Detailed instructions on overview page
  - Explore the jmol structures!
  - We'll have live quizzes during lectures - please engage
- PDF notes also on Learn if needed



# Test poll!



## How do you like to engage with lectures?

You can select multiple choices

Take notes on paper

Listen

Other

Submit



# Results

**wooclap**

Quiz results will be available here  
after the lecture

# Let's get you thinking in 3D!

Picture a cube. Imagine touching one corner, and then also touch every corner that is two edges away from it.

**If you join those corners by lines, what shape do you get?**

Hexagon

Tetrahedron

-

Submit

# Results

**wooclap**

Quiz results will be available here  
after the lecture

# Lecture 1 Summary

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

# Introduction

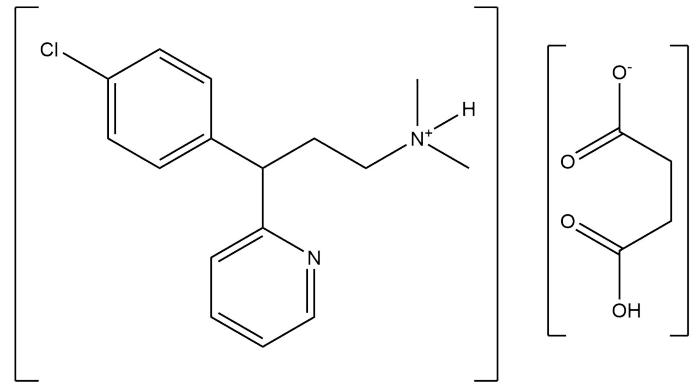
'Ionic materials' consist of both cations and anions:

- 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  $\text{NH}_4^+\text{CH}_3\text{COO}^-$
  - chlorpheniramine maleate (active part of Piriton®)

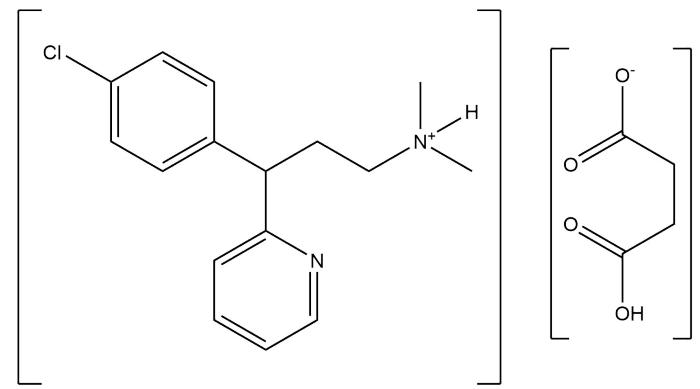


Chlorpheniramine maleate

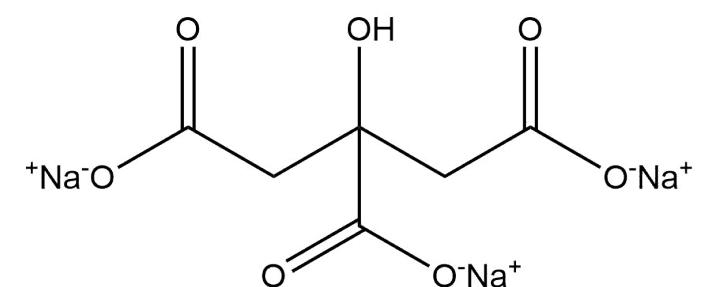
# Introduction

'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  $\text{NH}_4^+\text{CH}_3\text{COO}^-$
  - chlorpheniramine 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



Chlorpheniramine maleate

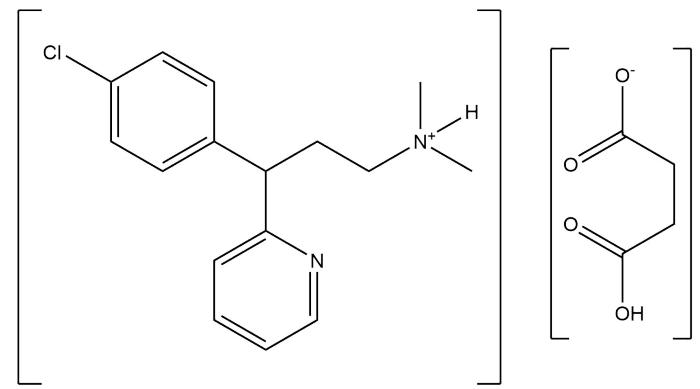


Trisodium Citrate ( $x=3$ )

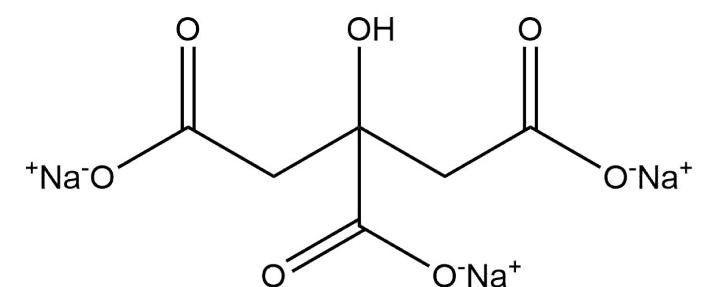
# Introduction

'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  $\text{NH}_4^+\text{CH}_3\text{COO}^-$
  - chlorpheniramine 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



Chlorpheniramine 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?

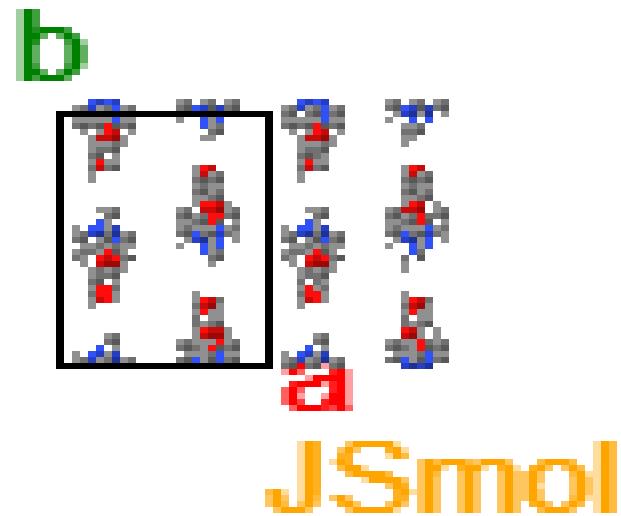
- Large range of practical applications
  - important for energy storage, but lots of other applications!
  - ionic liquids are gaining attention for many applications
- High melting points due to Coloumbic energy (see [later](#))
- Electrically insulating
  - Electronegativity differences promote localised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

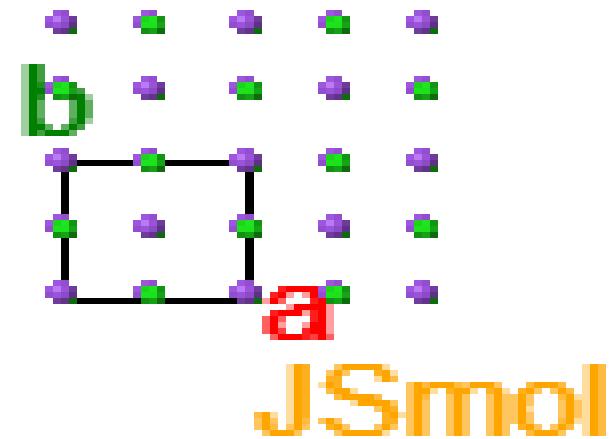
## Molecular (e.g. paracetamol)

- Strong intramolecular bonds
- Weaker intermolecular interactions



## Infinite (e.g. NaCl)

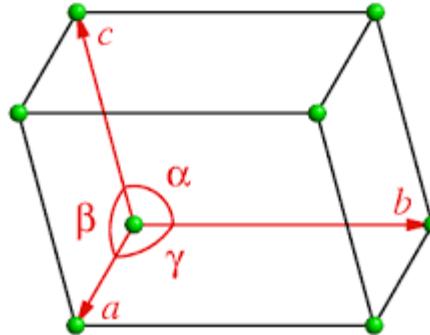
- Strong bonds between all atoms
- No discrete molecules



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

# Recap on crystal structure

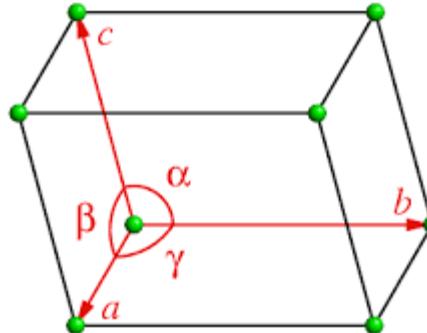
Periodic solids can be described by a unit cell



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

# Recap on crystal structure

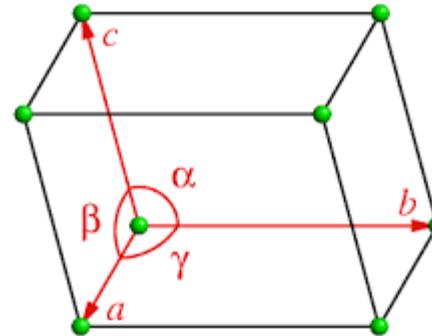
Periodic solids can be described by a unit cell



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

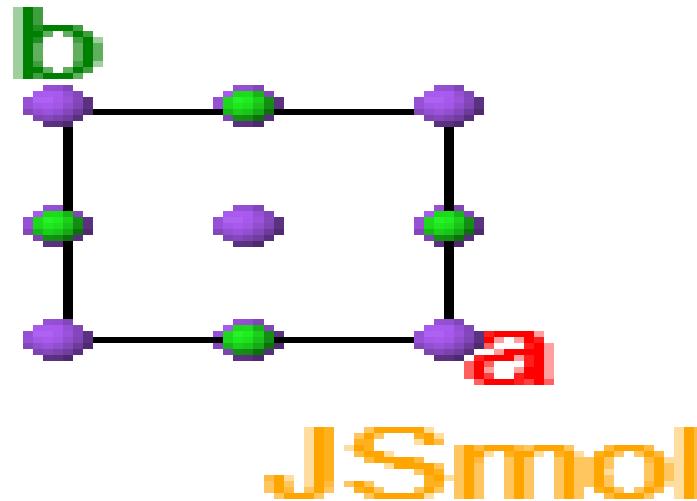
# Recap on crystal structure

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 of 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 <sub>h</sub> )	
Na atoms at:	(0 0 0)   (½ ½ 0)   (½ 0 ½)   (0 ½ ½)	(all symmetry-related)
Cl atoms at:	(½ 0 0)   (0 ½ 0)   (0 0 ½)   (½ ½ ½)	(all symmetry-related)

Because of symmetry, we only need to define one Na and one Cl position.

# 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

For example NaCl:



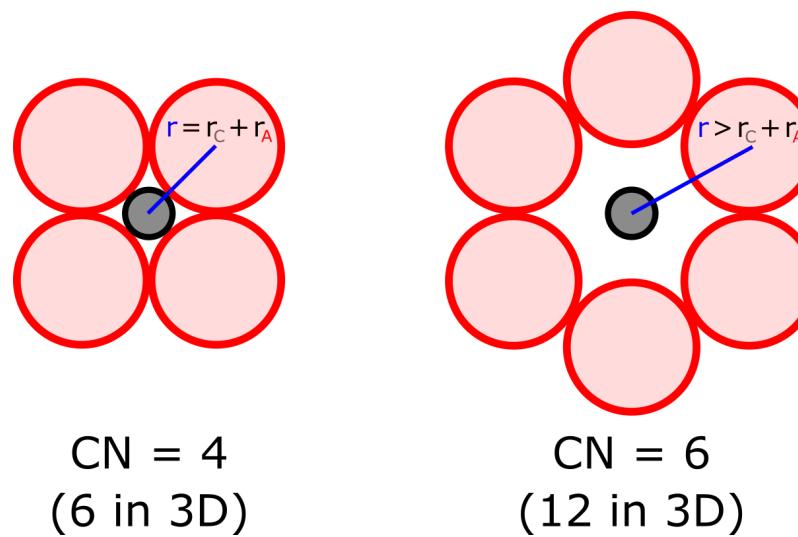
**JSmol**

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

# Ionic Structures

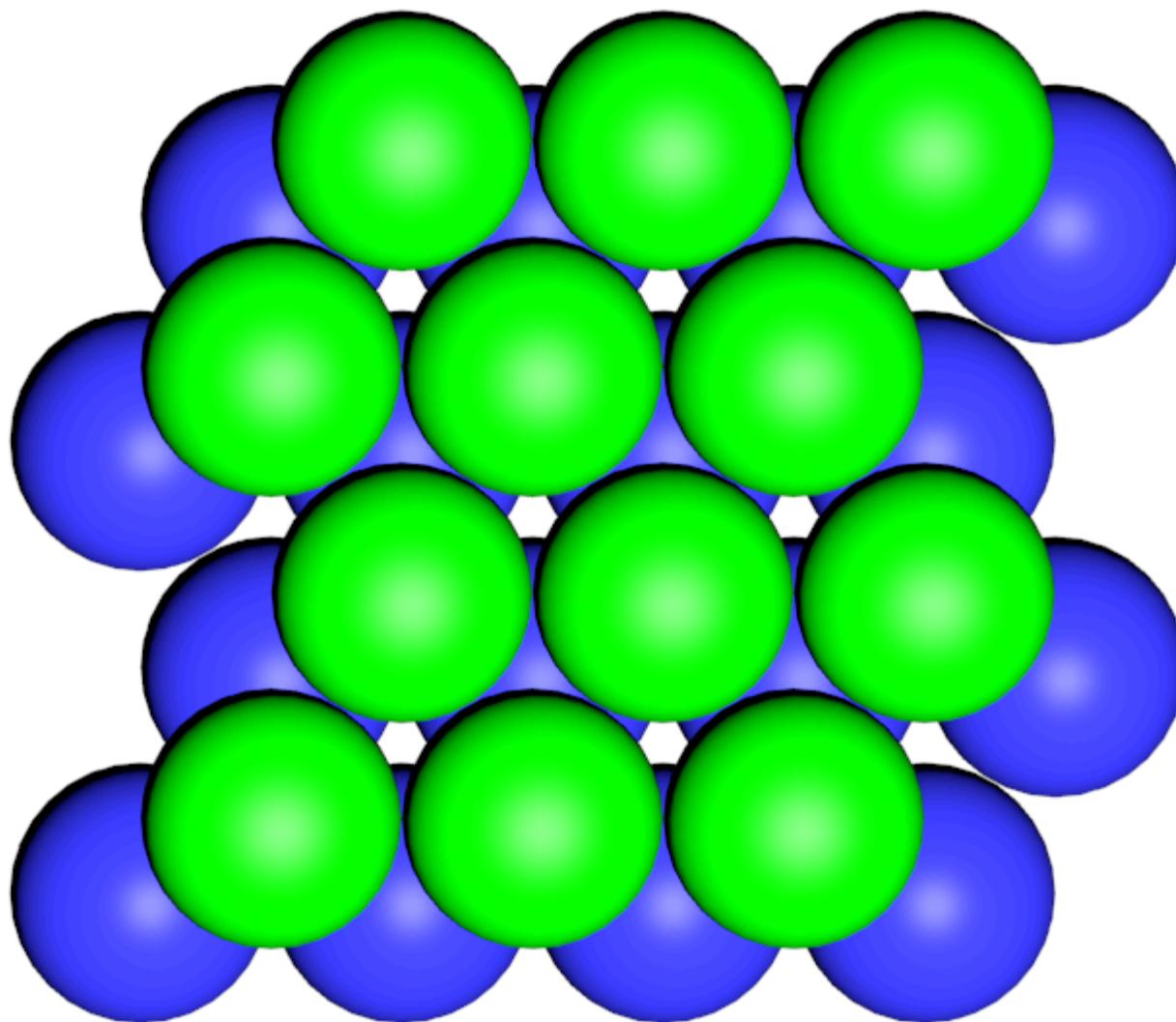
Generally, structures **maximise cation-anion** interactions (-ve energy) while **minimising like-charge** interactions (+ve energy)

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



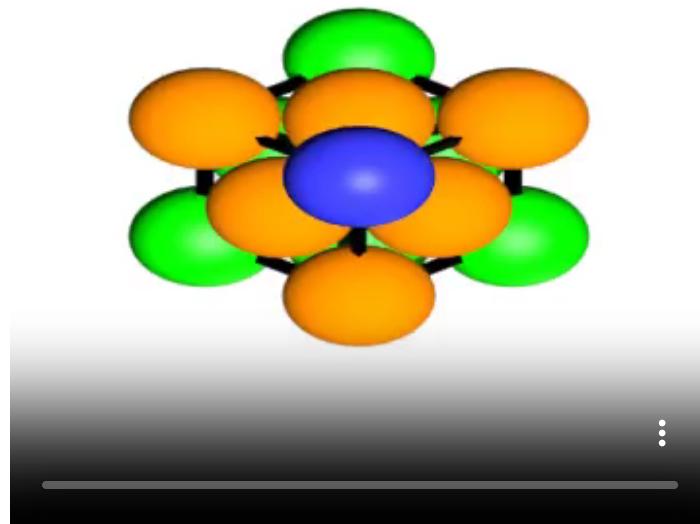
In many materials, the optimum is found when the largest ion (often oxide) is **close-packed**

# Close packing

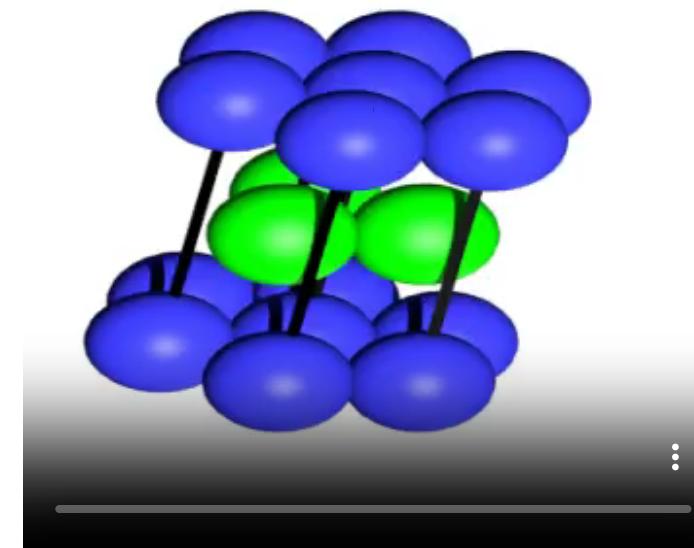


# Close packing

Face-centered cubic (FCC)  
... ABCABC ...

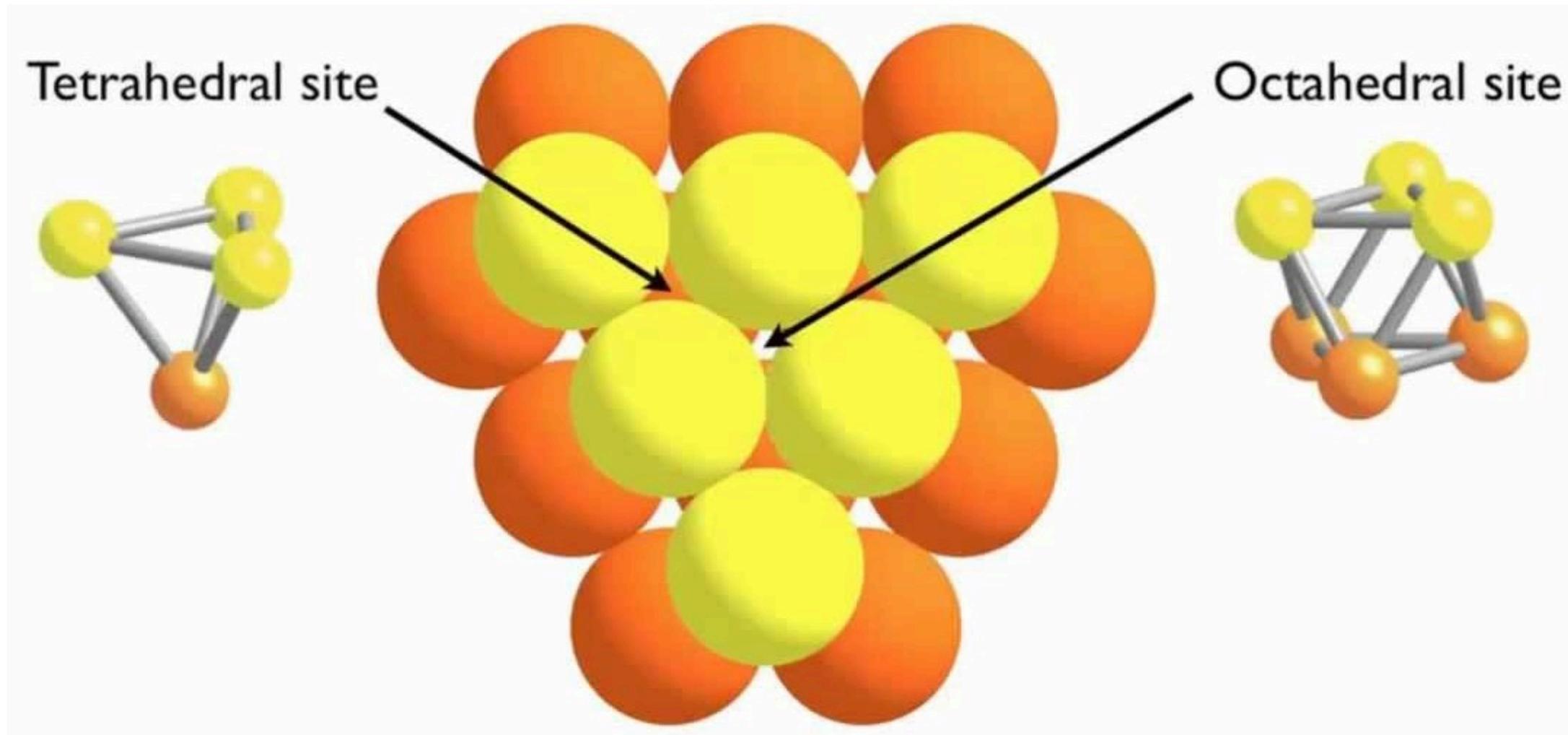


Hexagonal close-packed (HCP)  
... ABABAB ...



# Holes

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



# How are you getting on? Vote

**How confident do you feel about these topics?**  
**(5 = confident, 1 = completely lost)**

Unit cells and lattice parameters

1

2

3

4

5

Symmetry

1

2

3

4

5

Submit

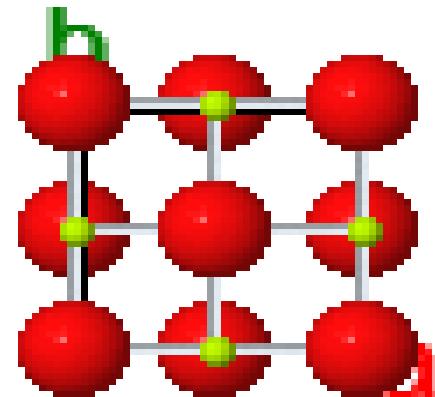
How are you getting on? Results

**wooclap**

Quiz results will be available here  
after the lecture

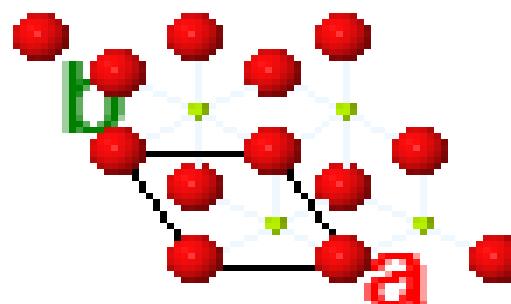
# Octahedral holes

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



**JSmol**

Rock salt (NaCl) structure



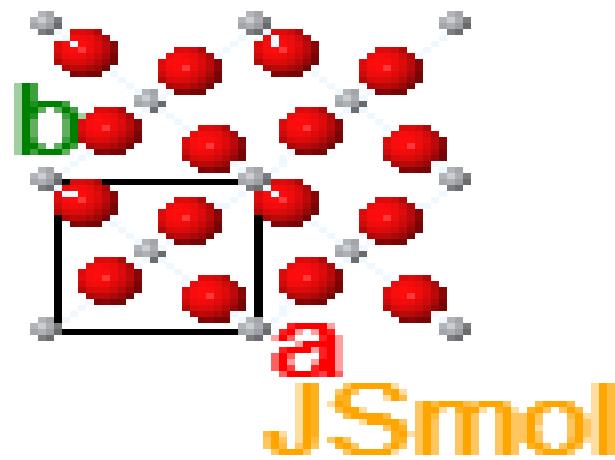
**JSmol**

Nickel Arsenide structure (e.g. FeS)



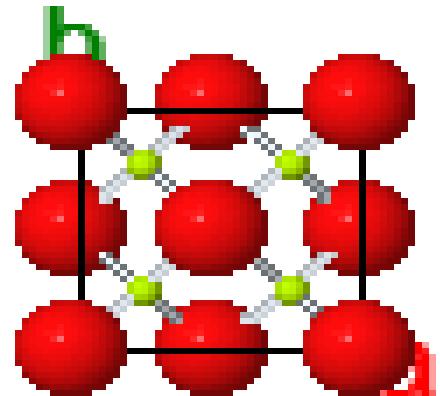
# Rutile

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

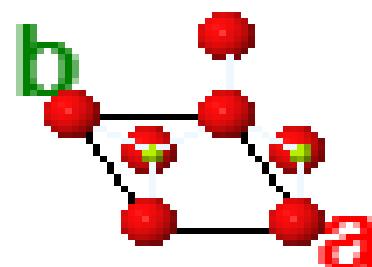


# Tetrahedral holes

Two **holes** per cp ion



JSmol



JSmol

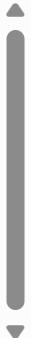
Holes filled	FCC Type	CN(A/X)	HCP Type	CN(A/X)
All	Fluorite ( $\text{CaF}_2$ )	4/8	(not possible)	-
Half	Zinc-blende ( $\text{ZnS}$ )	4/4	Wurtzite ( $\text{ZnS}$ )	4/4

# 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...)

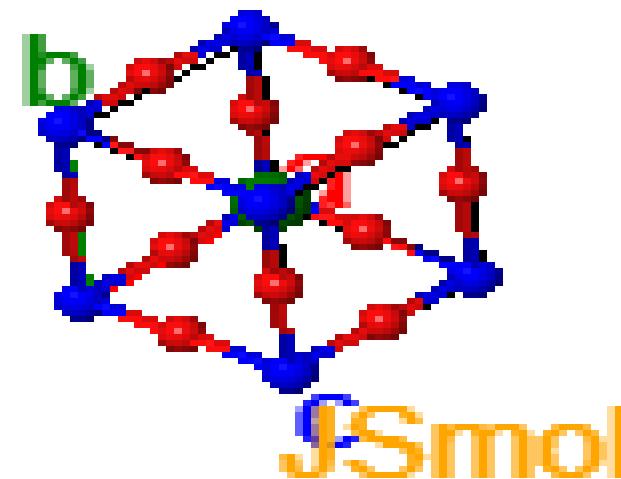
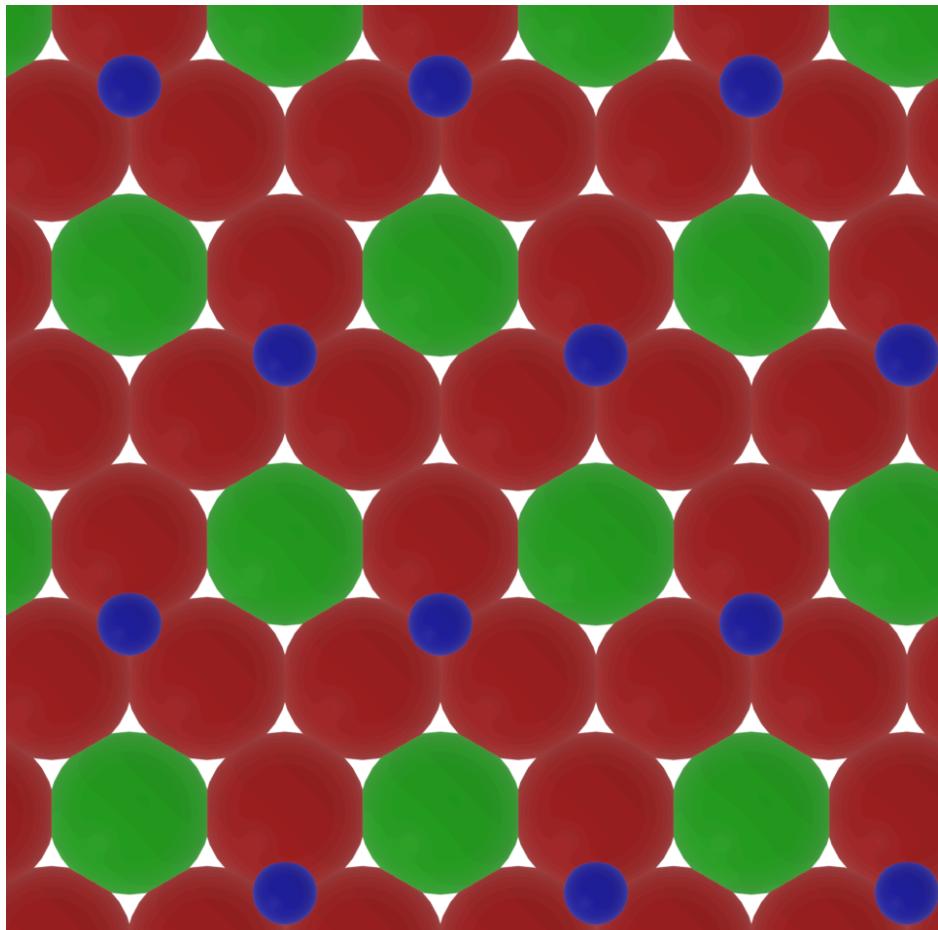
- Very difficult to predict!

# Beyond binary compounds

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

An important one is perovskite,  $\text{ABX}_3$

- $r(\text{A}) \simeq r(\text{X})$ , so can be considered as FCC  $\text{AX}_3$  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!

# Feedback



**What did you like or dislike about lecture 1?**

Write your answer...

You can answer multiple times



Submit



