Lecture 1 - Ionic structures

Return to course contents

Course Summary

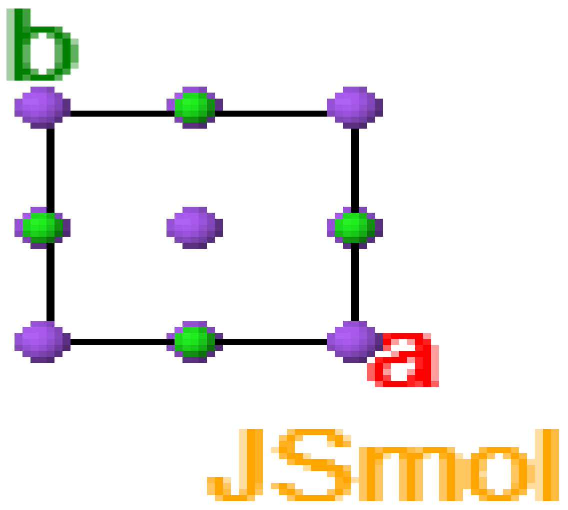
This course aims to introduce you to the importance of ionic materials in many applications.

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!

Mentimeter

What do you prefer to do during lectures?

Your ranking

Click or drop options

Unranked options

Other

Sleep!

Listen

Results

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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.

Mentimeter

If you join those corners by new edges, what shape do you get?

- Hexagon
- Tetrahedron
- Square
- Triangle

Results

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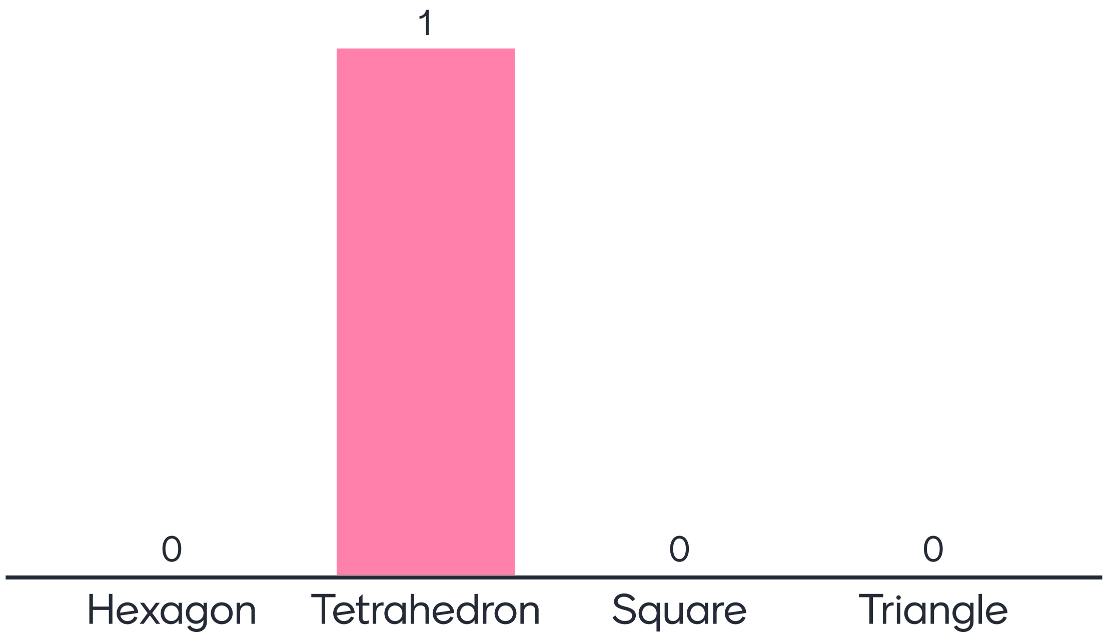

Lecture 1 Summary

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

Introduction

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- Many inorganic solids
  - e.g. $\mathrm{Na^+Cl^-}$ and $\mathrm{Mg^{2+}SO_4^{2-}}$

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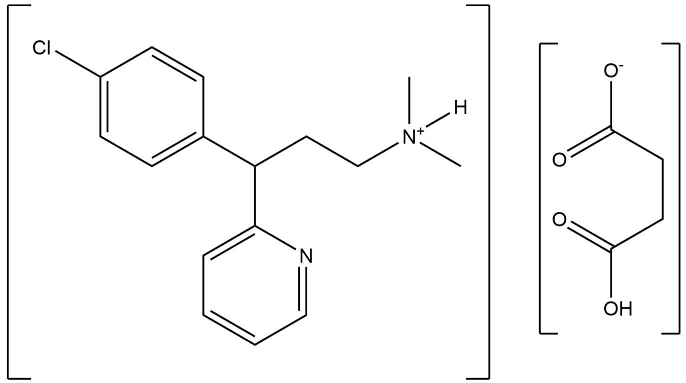
- Organic salts
  - ammonium acetate $\mathrm{NH_4^{+}CH_3COO^{-}}$
  - chlorphenirammonium maleate (active part of Piriton®)



Chlorphenirammonium maleate

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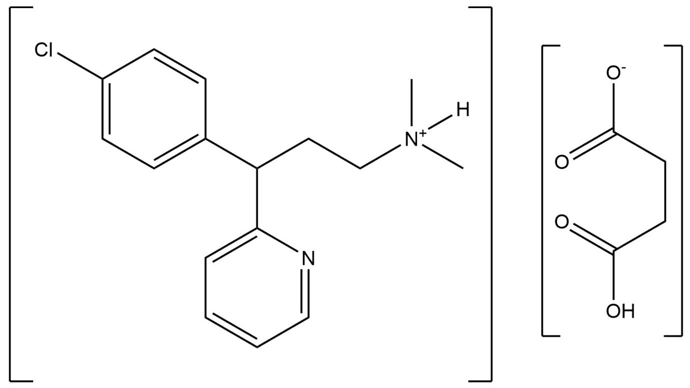
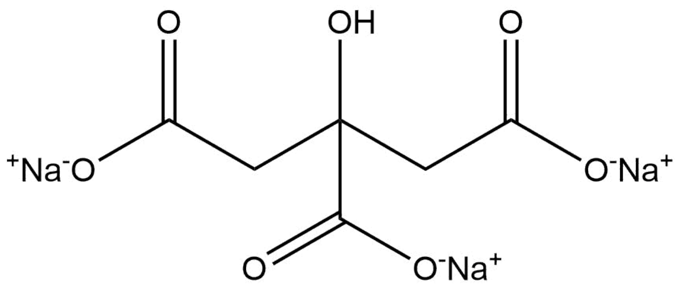
- (in)organic salts
  - Mono-/Di-/Tri-Sodium citrate $Na_xC_6H_{8-x}O_7$
    - collectively used as E331 in food
    - x can be varied from 1–3



Chlorphenirammonium maleate



Trisodium Citrate (x=3)

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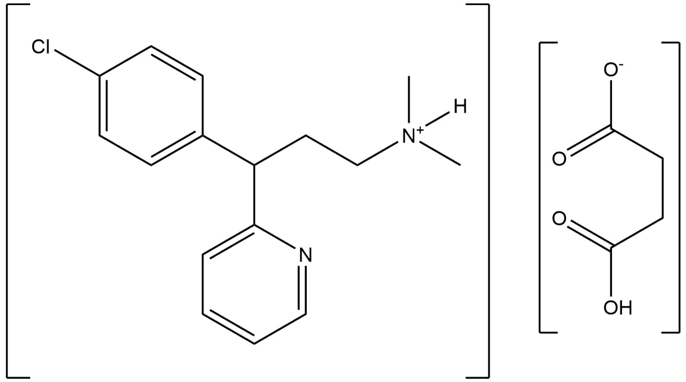
- Ionic liquids
  - Either organic or inorganic, liquid below 100 °C



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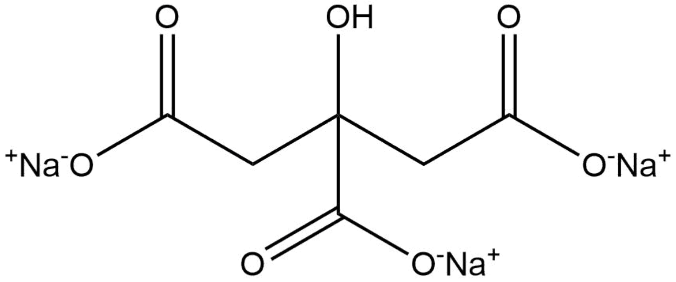

Trisodium Citrate (*x*=3)

Why are they interesting?

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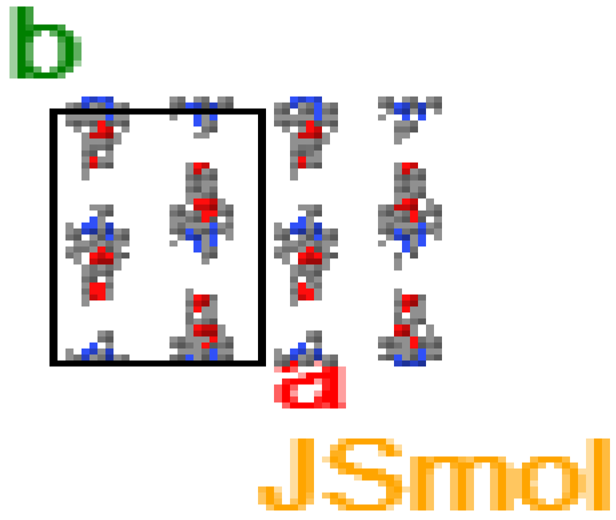
- High melting points due to Coloumbic energy (see later)
- Electrically insulating
  - Electronegativity differences promote localised electrons
- Usually hard, and often robust to harsh conditions
  - e.g. Synroc* is used to encapsulate nuclear waste

We can divide solids into two categories:

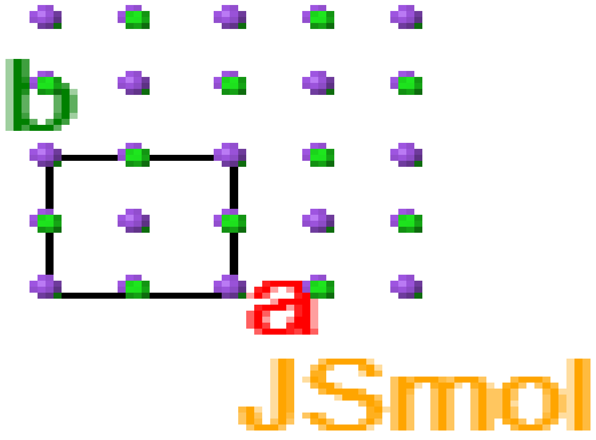
Molecular (e.g. paracetamol)

- Strong intramolecular bonds
- Weaker intermolecular interactions



Infinite (e.g. NaCl)

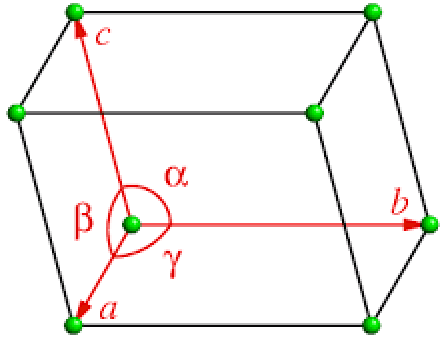
- Strong bonds between all atoms
- No discrete molecules



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 (α, β, γ)
  - 'Lattice parameters'

Recap on crystal structure

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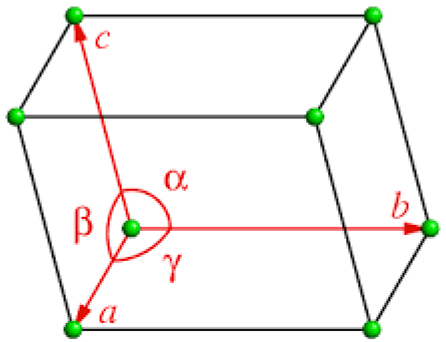

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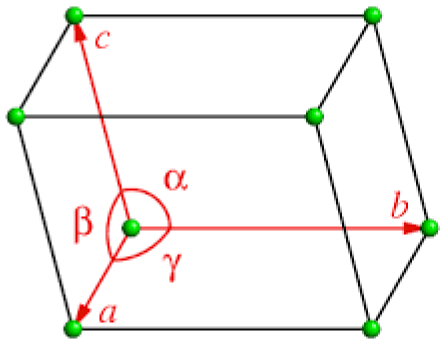

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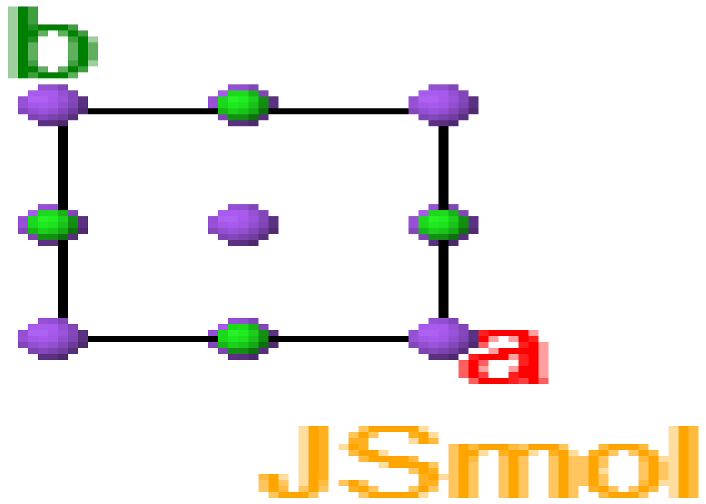
  - 'Lattice parameters'
- Possesses 'space group' symmetry (an extension of point groups)
- Atom positions defined by fractional position along lattice directions

Example: Sodium chloride



Cubic structure	$a = b = c = 5.62$ Å, $\alpha = \beta = \gamma = 90^\circ$				
Spacegroup	$\mathrm{Fm\bar{3}m}$ (#225, point group = $\mathrm{O_h}$)				
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

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

see Chemistry 1 "States of Matter" for a recap on ionic compounds

Infinite summations

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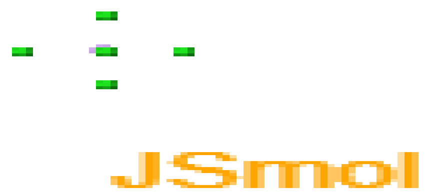
For example NaCl:

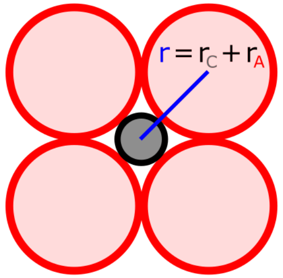


$$
\begin{aligned}
E_{\text{Madelung}} &= \sum_{i \neq j} \frac{q_i q_j}{4\pi\epsilon_0 r} \\
&= \frac{\mathrm{N_A} q_i q_j}{4\pi\epsilon_0 r}\left(6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{2} + \frac{24}{\sqrt{5}} - \dots\right) \\
&\simeq \frac{\mathrm{N_A} q_i q_j}{4\pi\epsilon_0 r}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

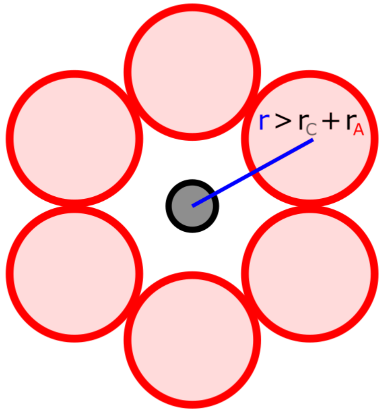
Ionic Structures

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



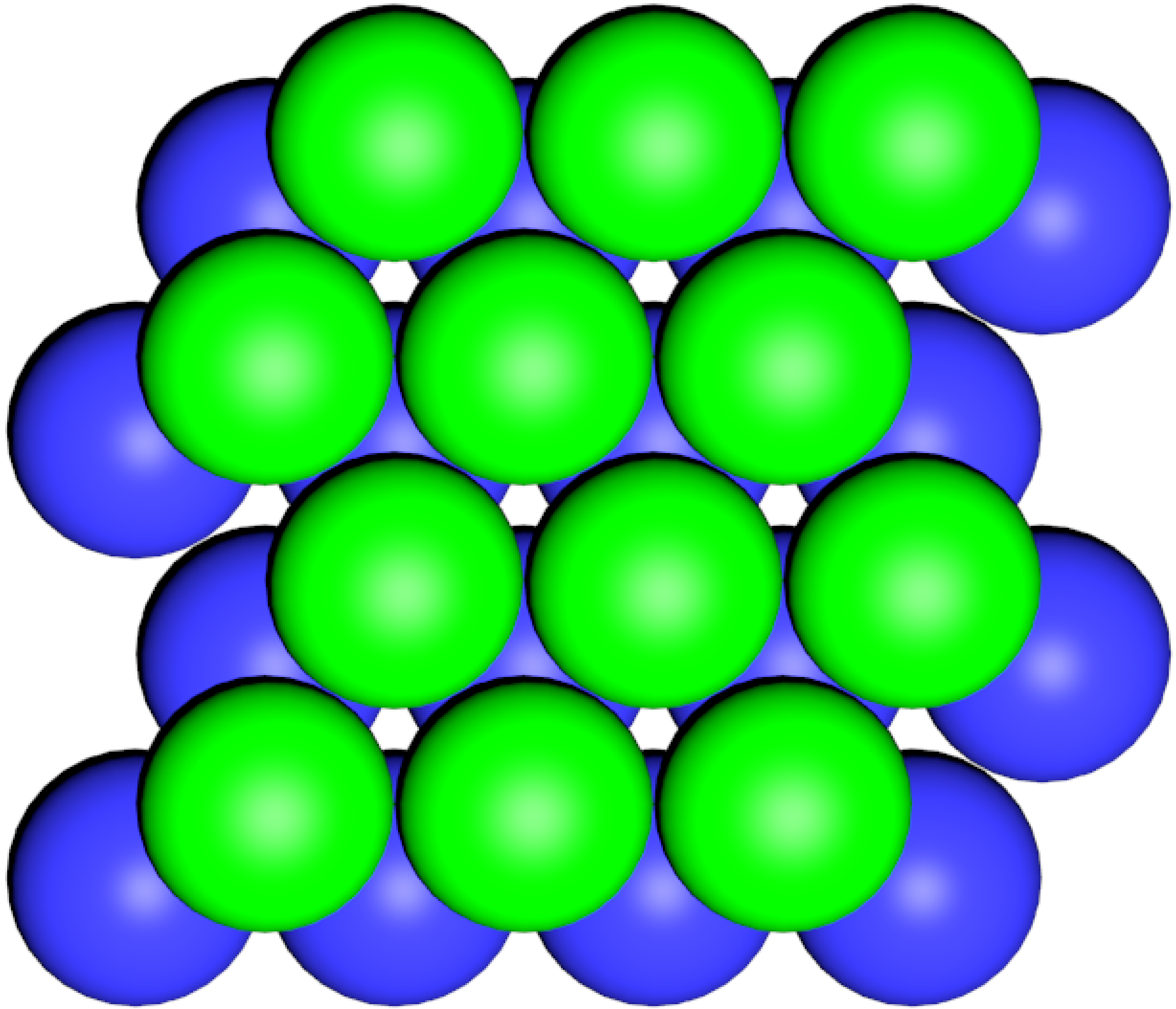
CN = 4
(6 in 3D)



CN = 6
(12 in 3D)

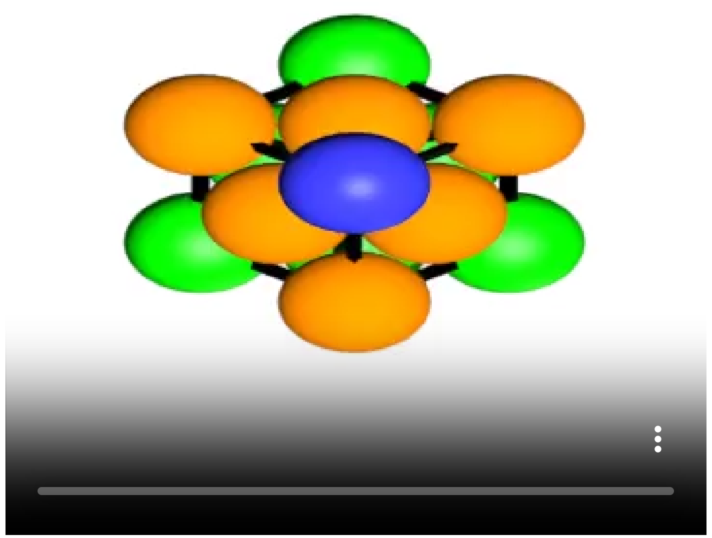
In many materials, the optimum is found when the largest ion (often oxide) is **close-packed**

Close packing

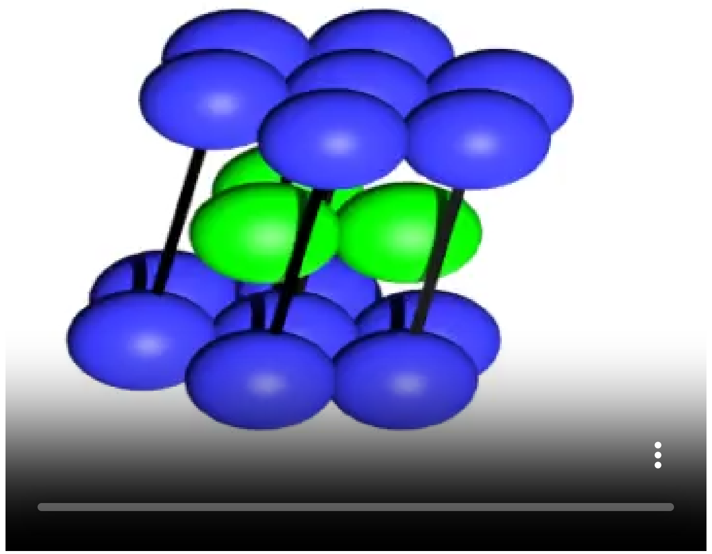


Close packing

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

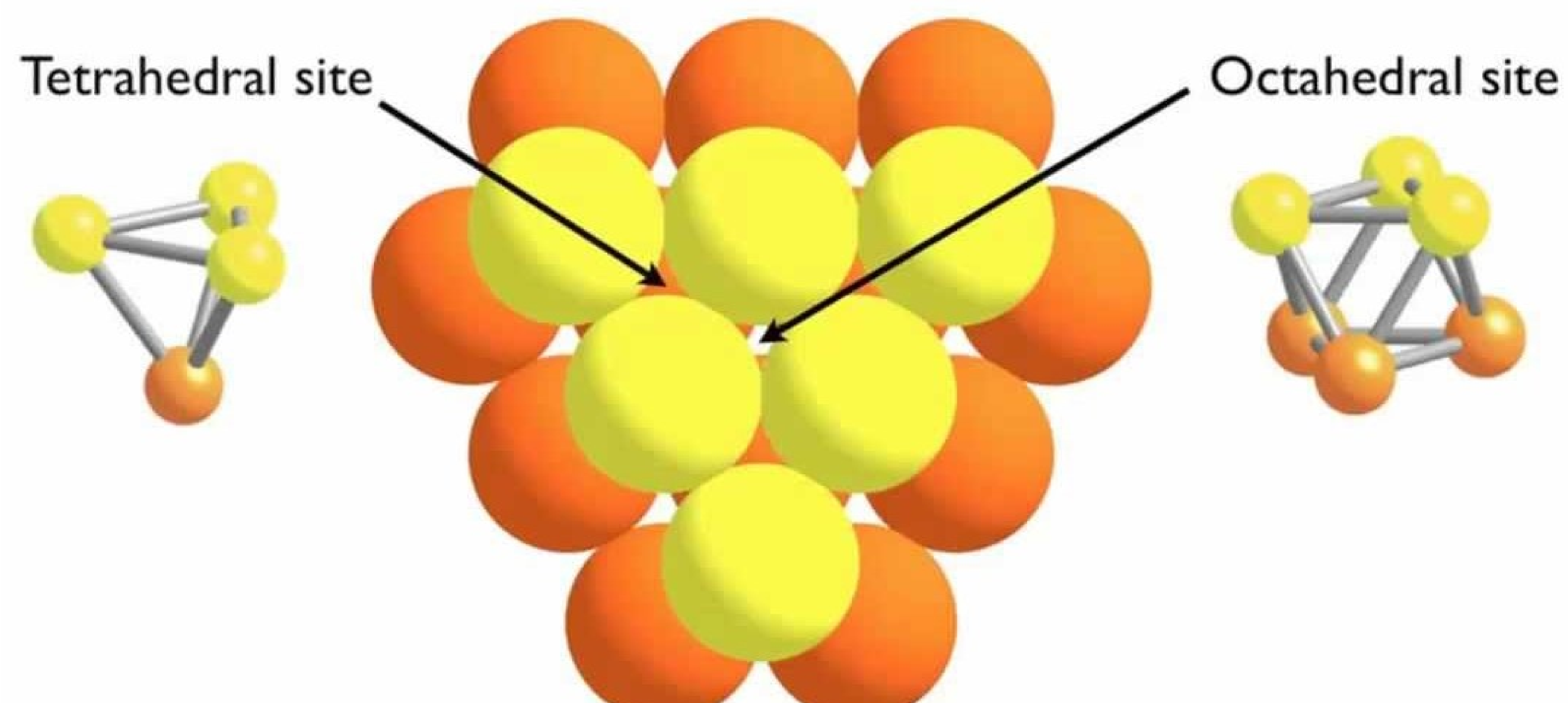


Hexagonal close-packed (HCP)
... ABABAB ...



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

Mentimeter

How confident do you feel about...

Unit cells and lattice parameters Skip

1 Completely lost

1 5

Completely lost Really confident

Symmetry Skip

1 Completely lost

1 5

Completely lost Really confident

Close packing Skip

1 Completely lost

How are you getting on? Results

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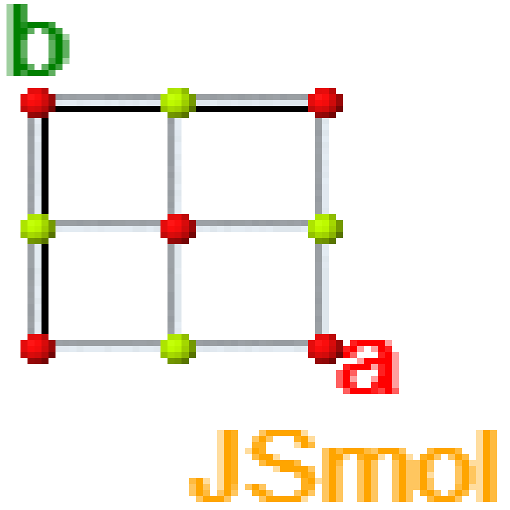
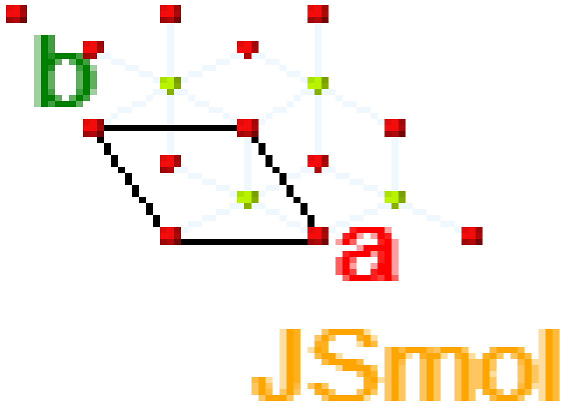
Octahedral holes

One hole per cp ion - both are 6-coordinate



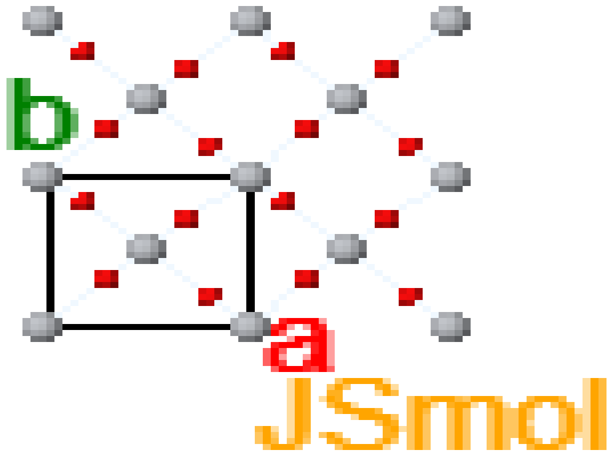
Rock salt (NaCl) structure



Nickel Arsenide structure (e.g. FeS)

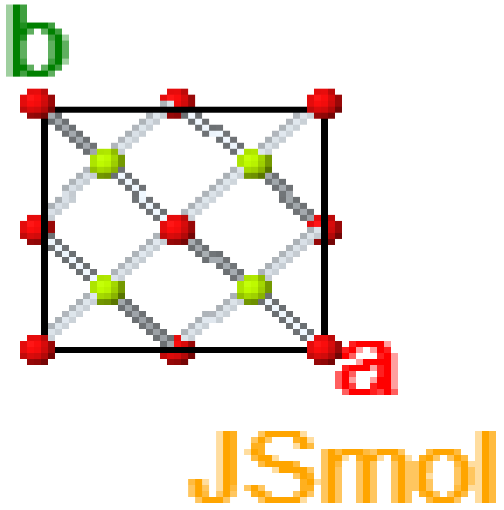
Rutile

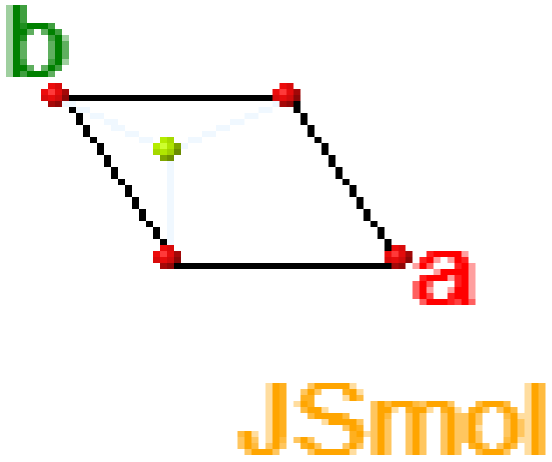
Although not strictly close-packed, rutile (TiO_2) is distorted HCP with Ti^{4+} filling half the octahedral holes CN = 6 / 3



Tetrahedral holes

Two holes per cp ion





Holes filled	FCC Type	CN(A/X)		HCP Type	CN(A/X)
All	Fluorite (CaF_2)	4/8		(not possible)	-
Half	Zinc-blende (ZnS)	4/4		Wurtzite (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_2 Structure**
0.7 - 1.0	8	$CsCl$	CaF_2
0.4 - 0.7	6	$NaCl$	TiO_2
0.2 - 0.4	4	ZnS (Wurtzite/Zinc-blende)	Anti-fluorite (e.g. Li_2S)

These are only approximate 'rules', and other binary structures exist (e.g. CdI_2, $CdCl_2$, PbO, etc...)

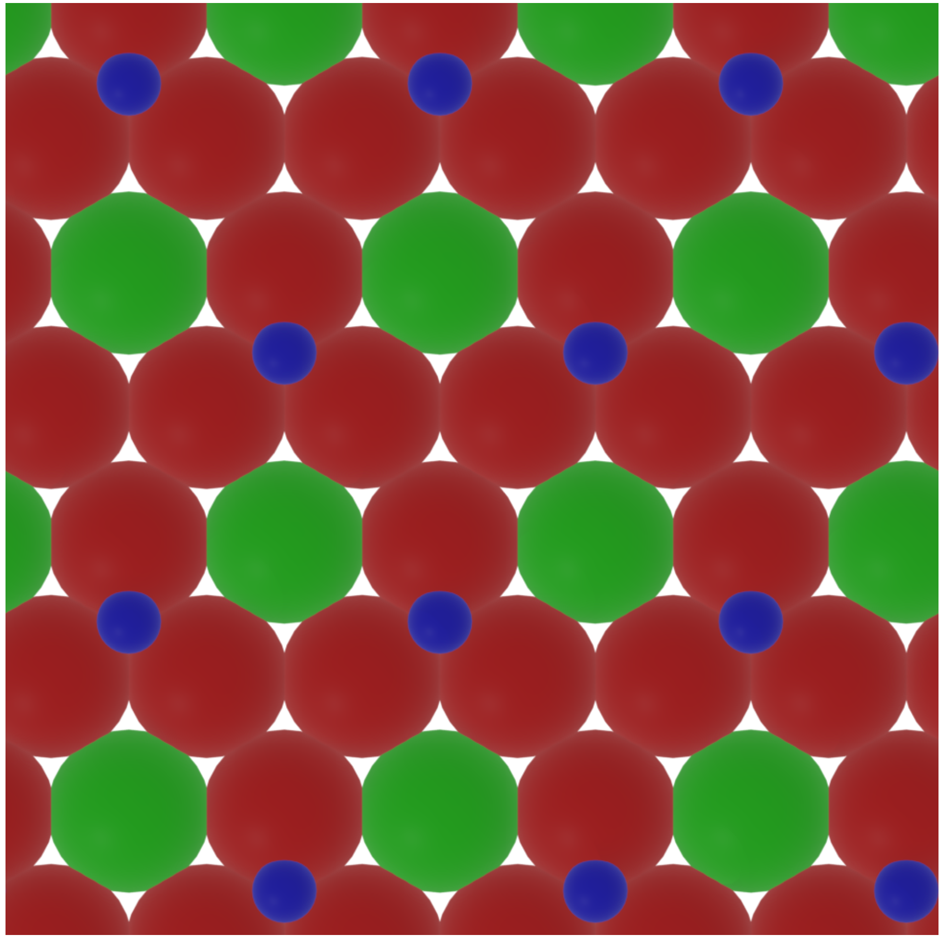
- Very difficult to predict!

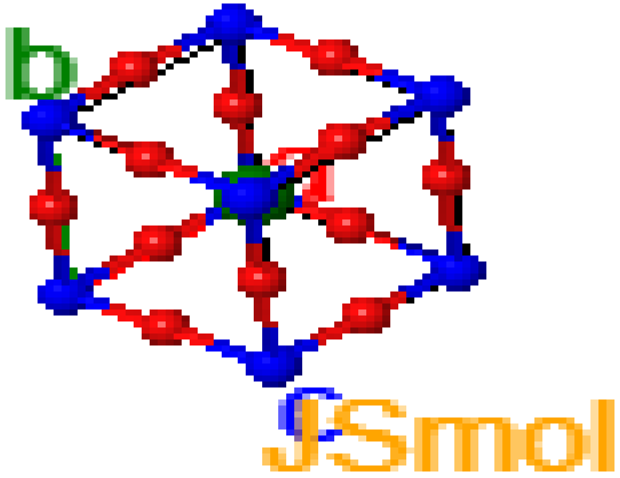
Beyond binary compounds

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

An important one is perovskite, $\mathrm{ABX_3}$

- $r(\mathrm{A}) \simeq r(\mathrm{X})$, so can be considered as FCC $\mathrm{AX_3}$ 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

Mentimeter

What did you like or dislike about this lecture?

Short answers are recommended. You have 200 characters left.

200

You can submit multiple responses

Submit