

Lecture 1 - Ionic structures

Course Summary

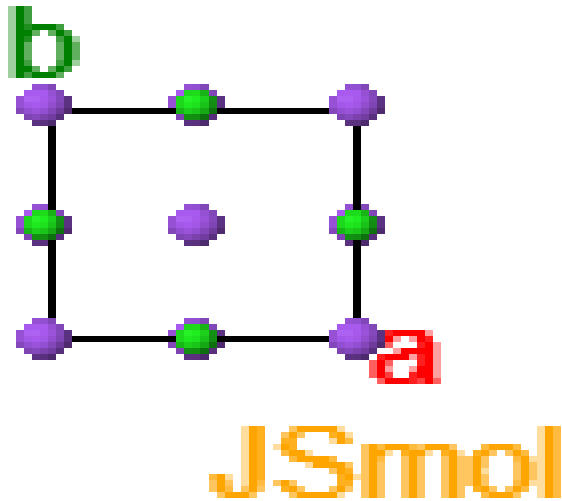
This course aims to introduce you to the importance of ionic materials in many applications.

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



 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



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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

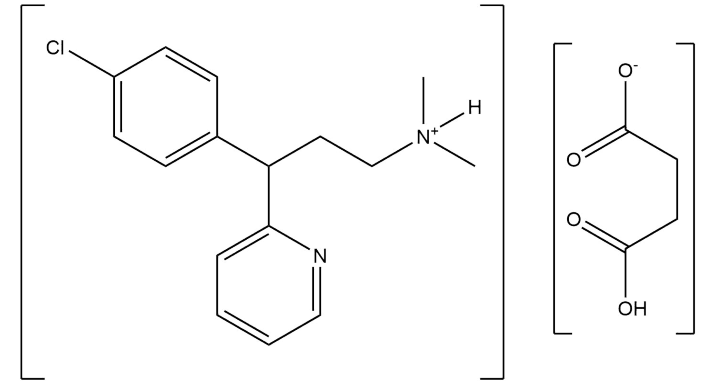
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- Many inorganic solids
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- Organic salts
 - ammonium acetate $\text{NH}_4^+ \text{CH}_3\text{COO}^-$
 - [chlorpheniraminium maleate](#) (active part of Piriton®)

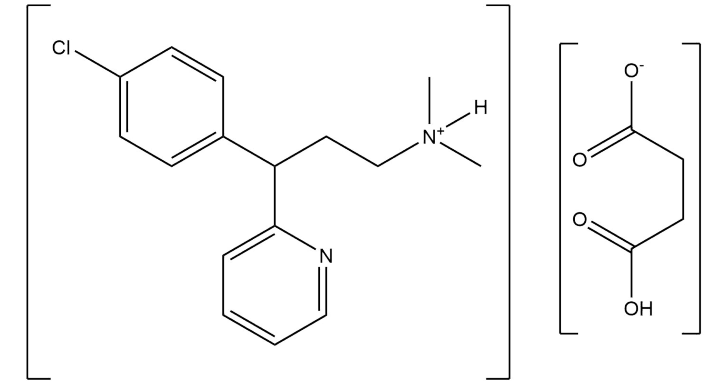


Chlorpheniraminium maleate

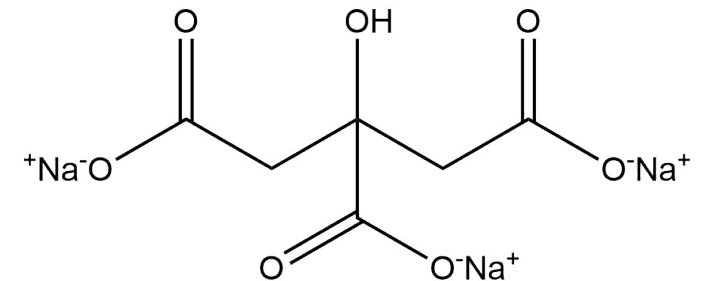
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- (in)organic salts
 - Mono-/Di-/Tri-Sodium citrate $\text{Na}_x\text{C}_6\text{H}_8-x\text{O}_7$
 - collectively used as E331 in food
 - x can be varied from 1–3



Chlorphenirammonium maleate

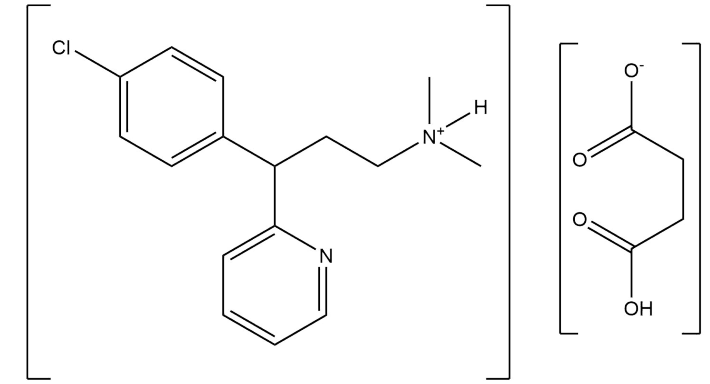


Trisodium Citrate (x=3)

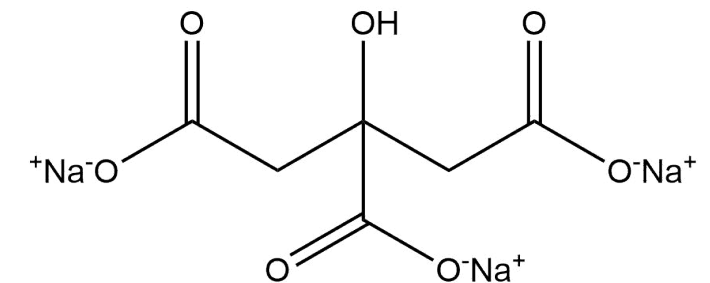
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 - x can be varied from 1–3
- Ionic liquids
 - Either organic or inorganic, liquid below 100 °C



Chlorphenirammonium maleate



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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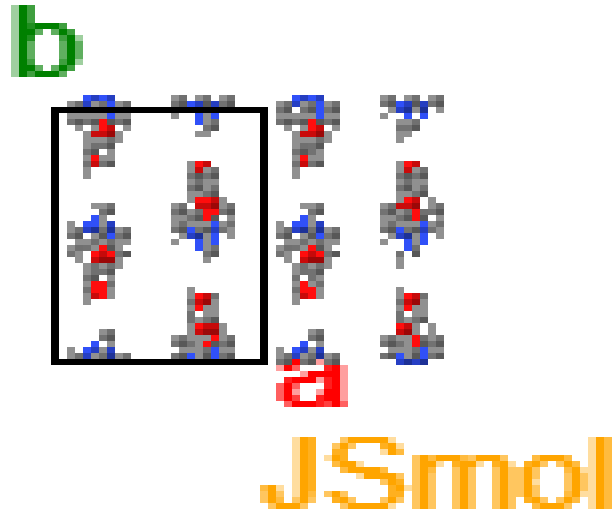
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- High melting points due to Coloumbic energy (see [later](#))
- Electrically insulating
 - Electronegativity differences promote localised electrons
- Usually hard, and often robust to harsh conditions
 - e.g. Synroc* is used to encapsulate nuclear waste



We can divide solids into two categories:

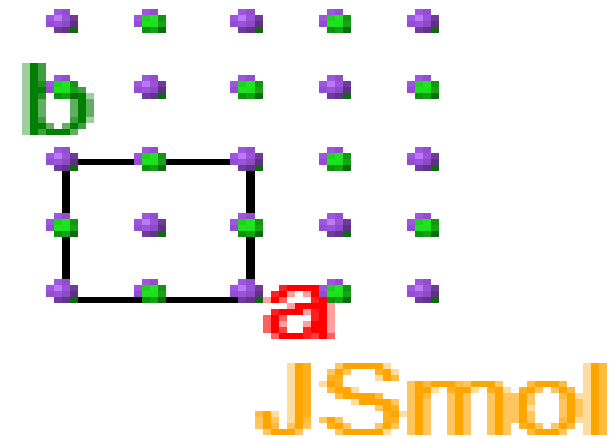
Molecular (e.g. paracetamol)

- Strong intramolecular bonds
- Weaker intermolecular interactions



Infinite (e.g. NaCl)

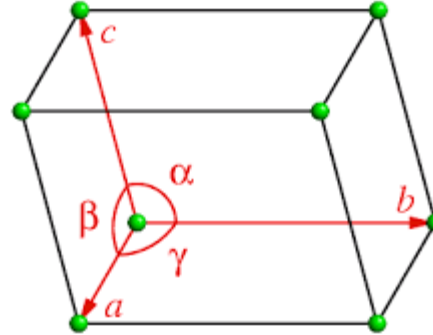
- Strong bonds between all atoms
- No discrete molecules



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

Recap on crystal structure

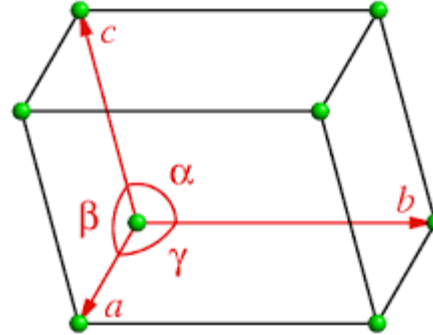
Periodic solids can be described by a unit cell



- Defined by lengths (a , b , c) and angles (α , β , γ)
 - 'Lattice parameters'

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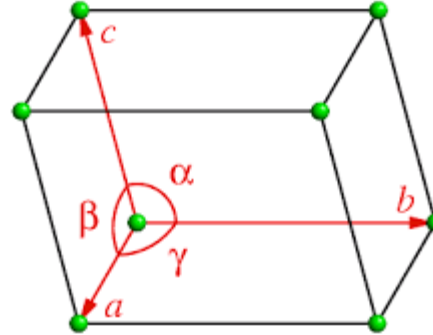
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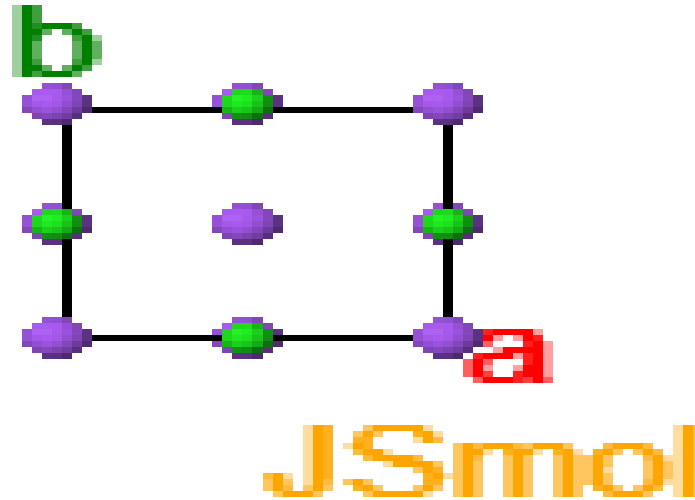
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- Defined by lengths (a, b, c) and angles (α, β, γ)
 - 'Lattice parameters'
- Possesses 'space group' symmetry (an extension of point groups)
- Atom positions defined by fractional position along lattice directions

Example: Sodium chloride



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

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

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- 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.

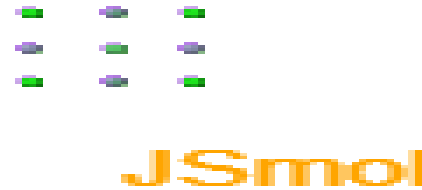
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For example NaCl:

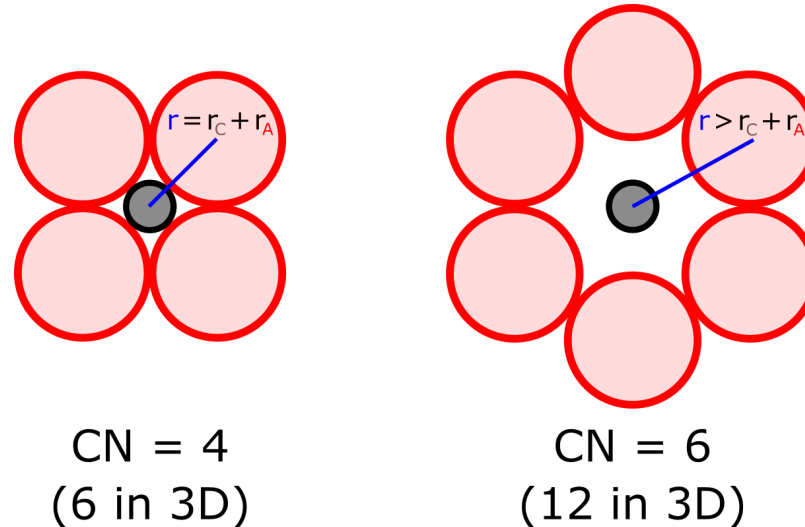


$$\begin{aligned} E_{\text{Madelung}} &= \sum_{i \neq j} \frac{q_i q_j}{4\pi\epsilon_0 r} \\ &= \frac{N_A q_i q_j}{4\pi\epsilon_0 r} \left(6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{2} + \frac{24}{\sqrt{5}} - \dots \right) \\ &\simeq \frac{N_A q_i q_j}{4\pi\epsilon_0 r} \times 1.74756 \end{aligned}$$

Ionic Structures

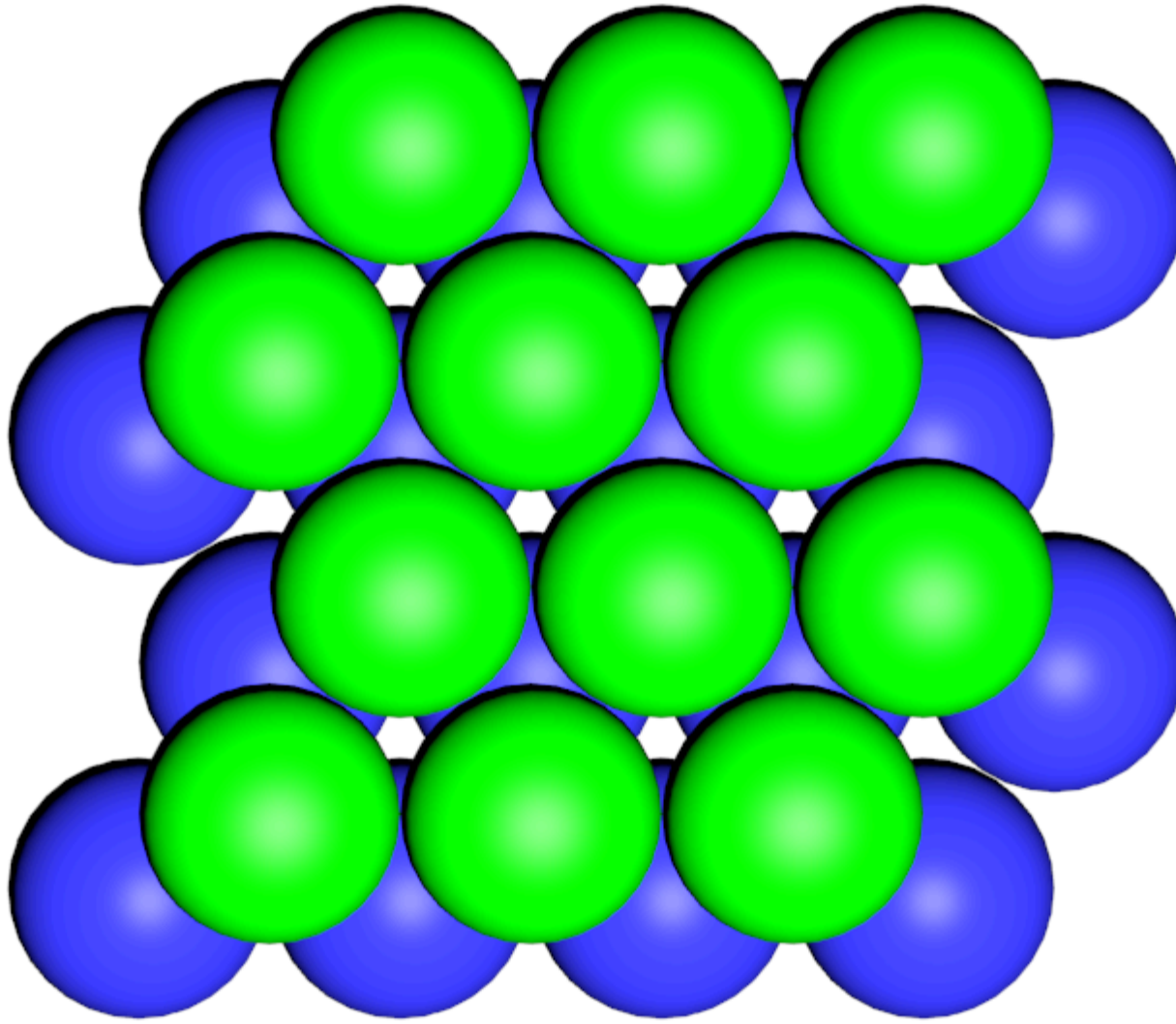
Generally, structures **maximise cation-anion** interactions (-ve energy) while **minimising like-charge** interactions (+ve energy)

- 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**

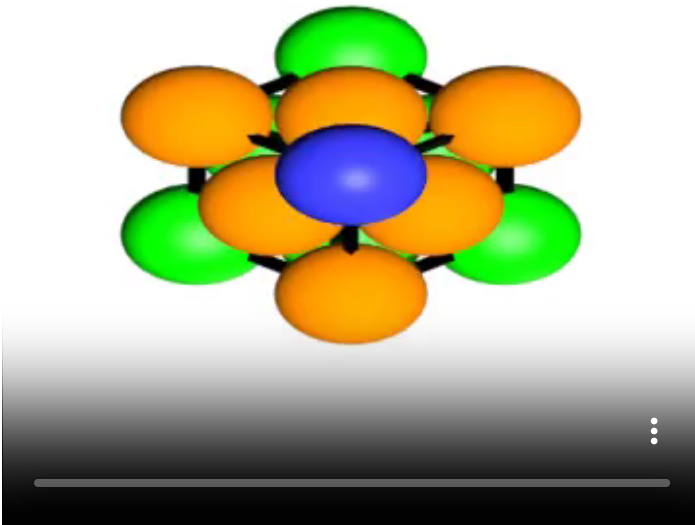
Close packing



Close packing

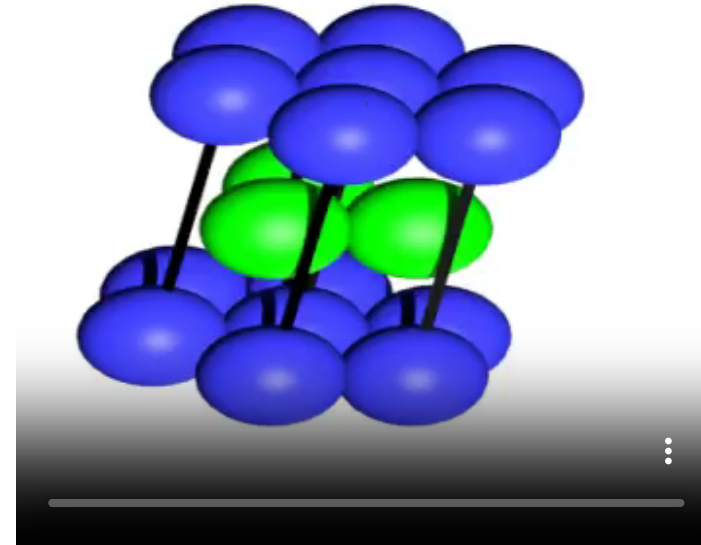
Face-centered cubic (FCC)

... ABCABC ...



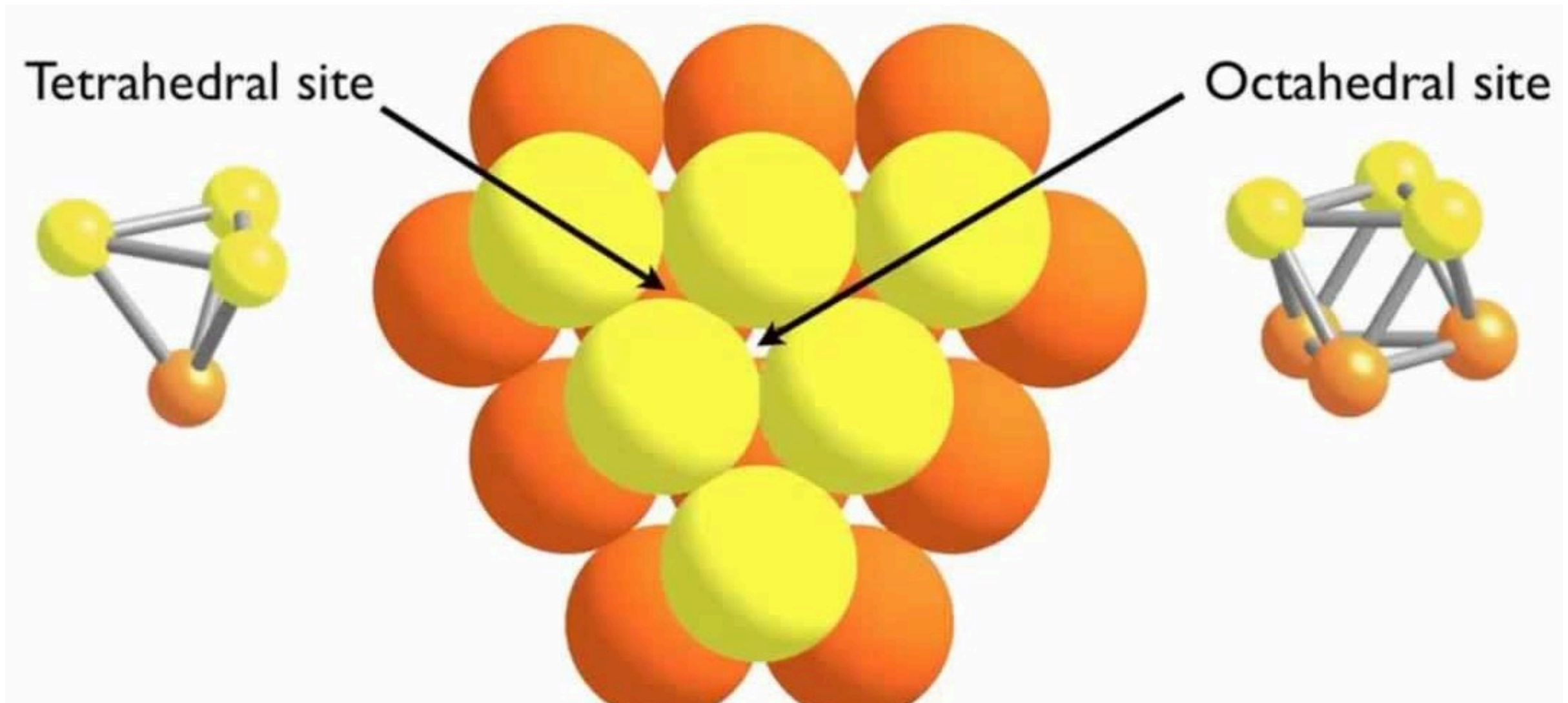
Hexagonal close-packed (HCP)

... 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



2

3

4

5

Symmetry



 Submit



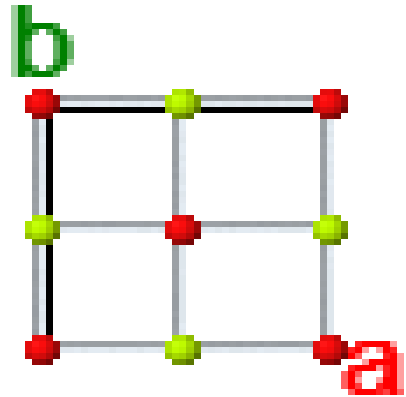
How are you getting on? Results

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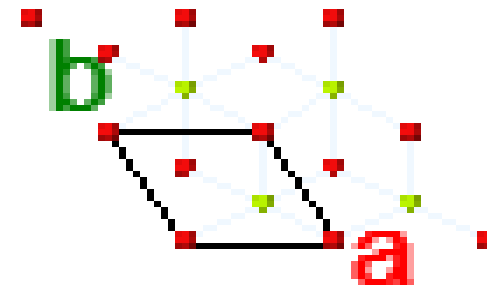
Octahedral holes

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



JSmol

Rock salt (NaCl) structure



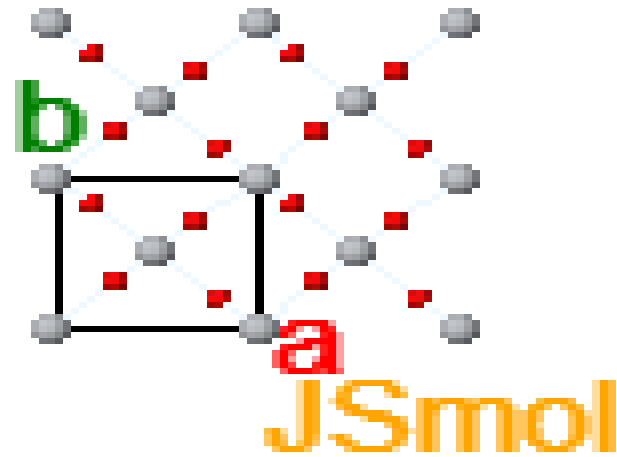
JSmol

Nickel Arsenide structure (e.g. FeS)



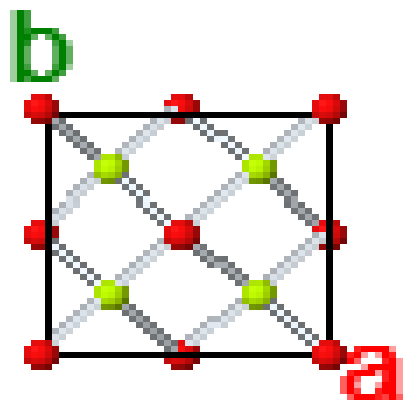
Rutile

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

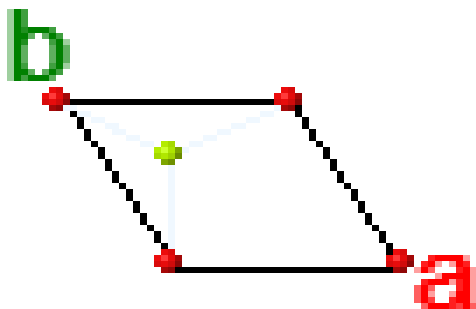


Tetrahedral holes

Two holes per cp ion



JSmol



JSmol

Holes filled	FCC Type	CN(A/X)	HCP Type	CN(A/X)
All	Fluorite (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 ₂ S)

These are only approximate 'rules', and other binary structures exist (e.g. CdI₂, CdCl₂, PbO, etc...)

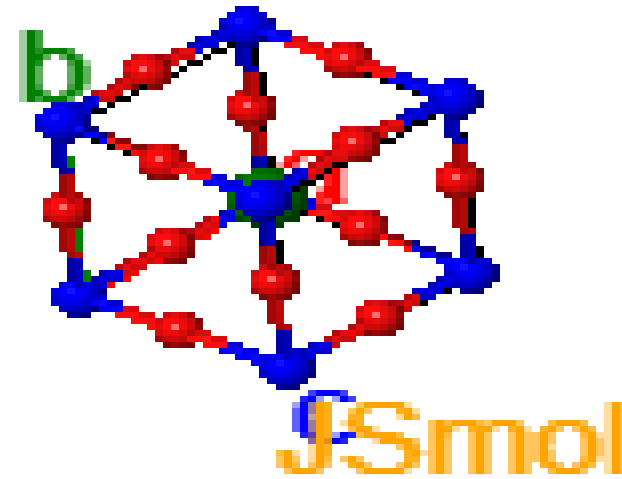
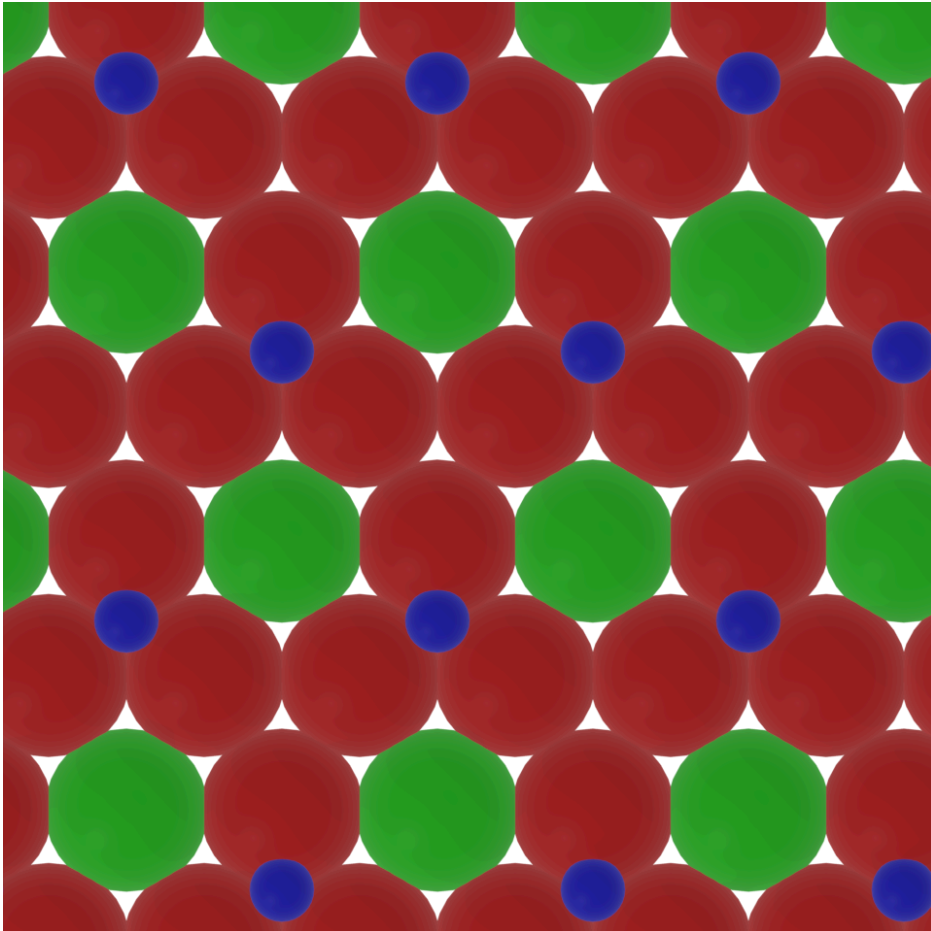
- Very difficult to predict!

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!

Feedback



What did you like or dislike about lecture 1?

Write your answer...

You can answer multiple times



 **Submit**



