Lecture 1 - Ionic structures

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Course Summary

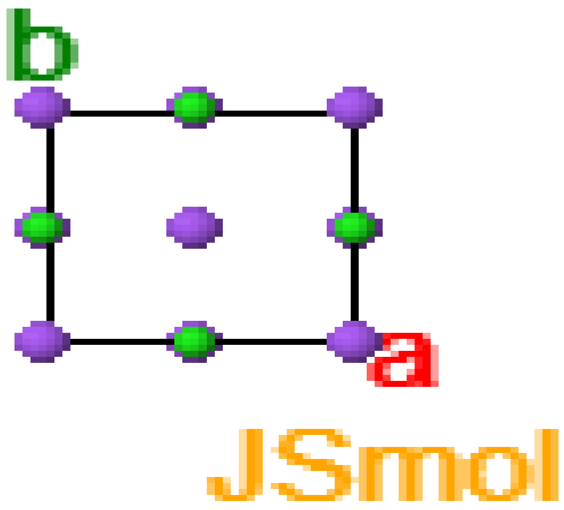
This course aims to introduce you to the importance of ionic materials in many applications.

What do I want you to do?

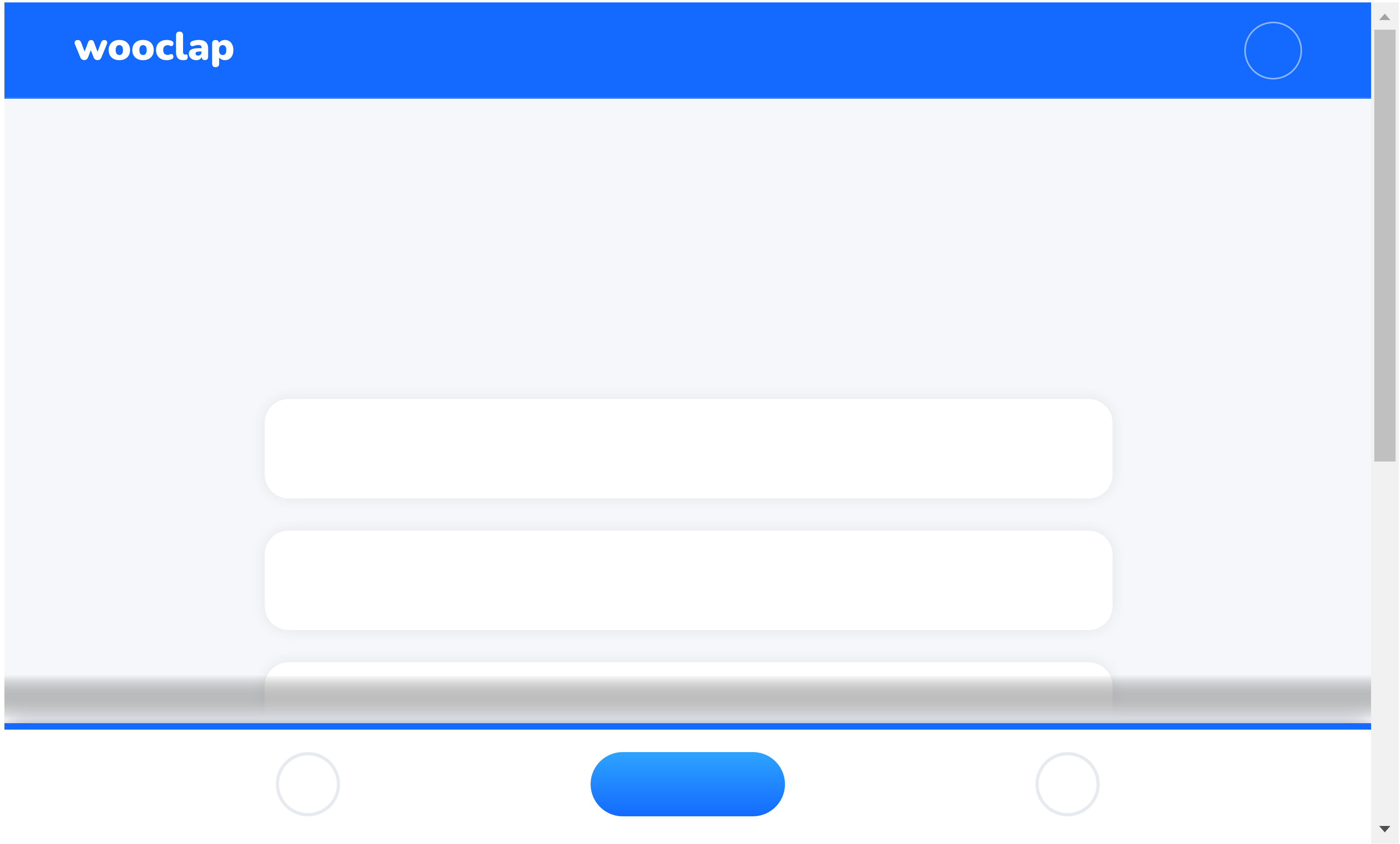
- Revise basic crystallography and ionic solids
- Try to understand examples, **don't memorise them**
- If in doubt - ask questions!

Lecture Notes

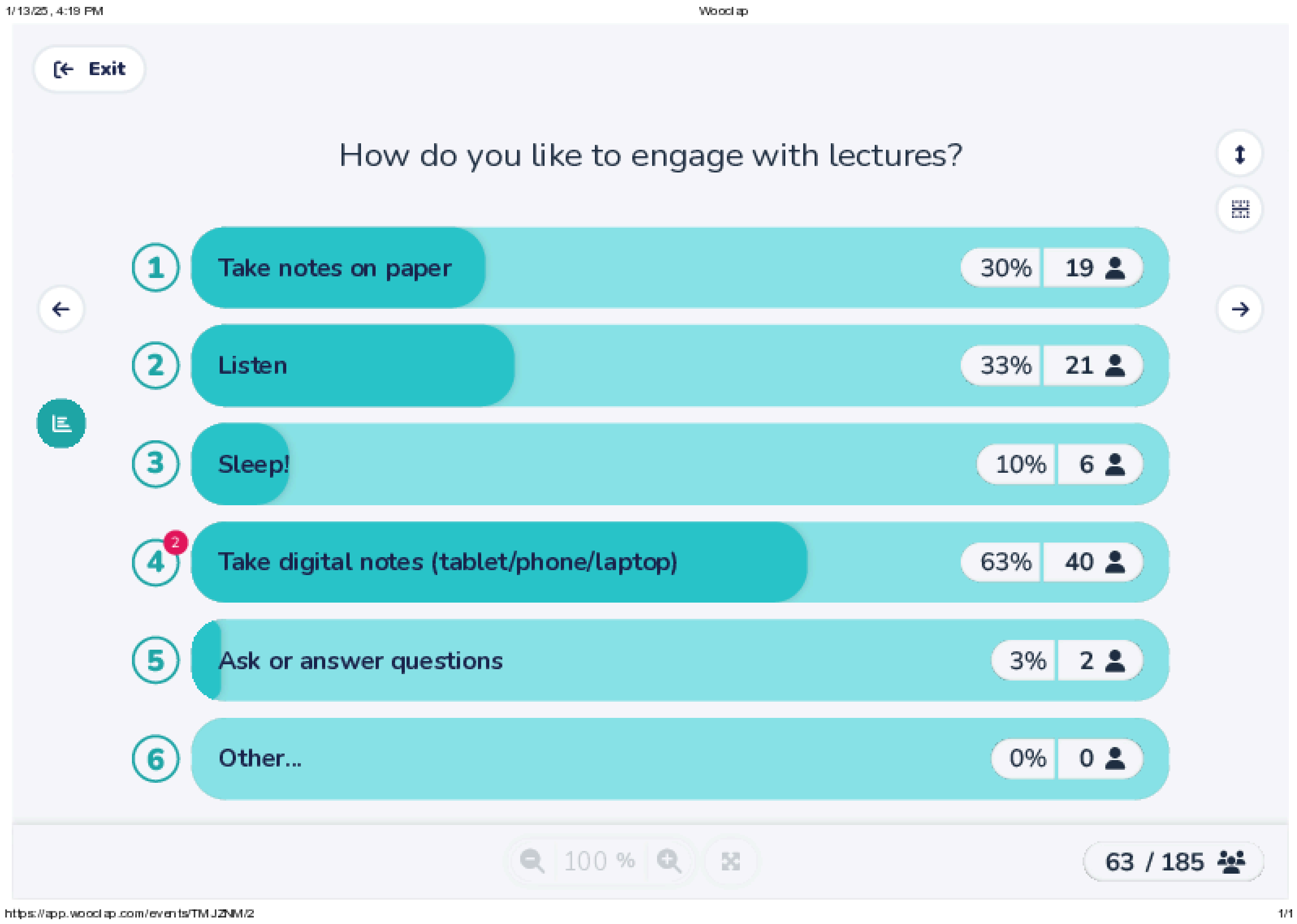
- Interactive HTML notes
  - Detailed instructions on overview page
  - Explore the jmol structures!
  - We'll have live quizzes during lectures - please engage
- PDF notes also on Learn if needed



Test poll!



Results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Exit
How do you like to engage with lectures?
1
Take notes on paper
30%
19
2
Listen
33%
21
3
Sleep!
10%
6
4
2
Take digital notes (tablet/phone/laptop)
63%
40
5
Ask or answer questions
3%
2
6
Other...
0%
0
100 %
63 / 185
https://app.wooclap.com/events/TMJZNM/2
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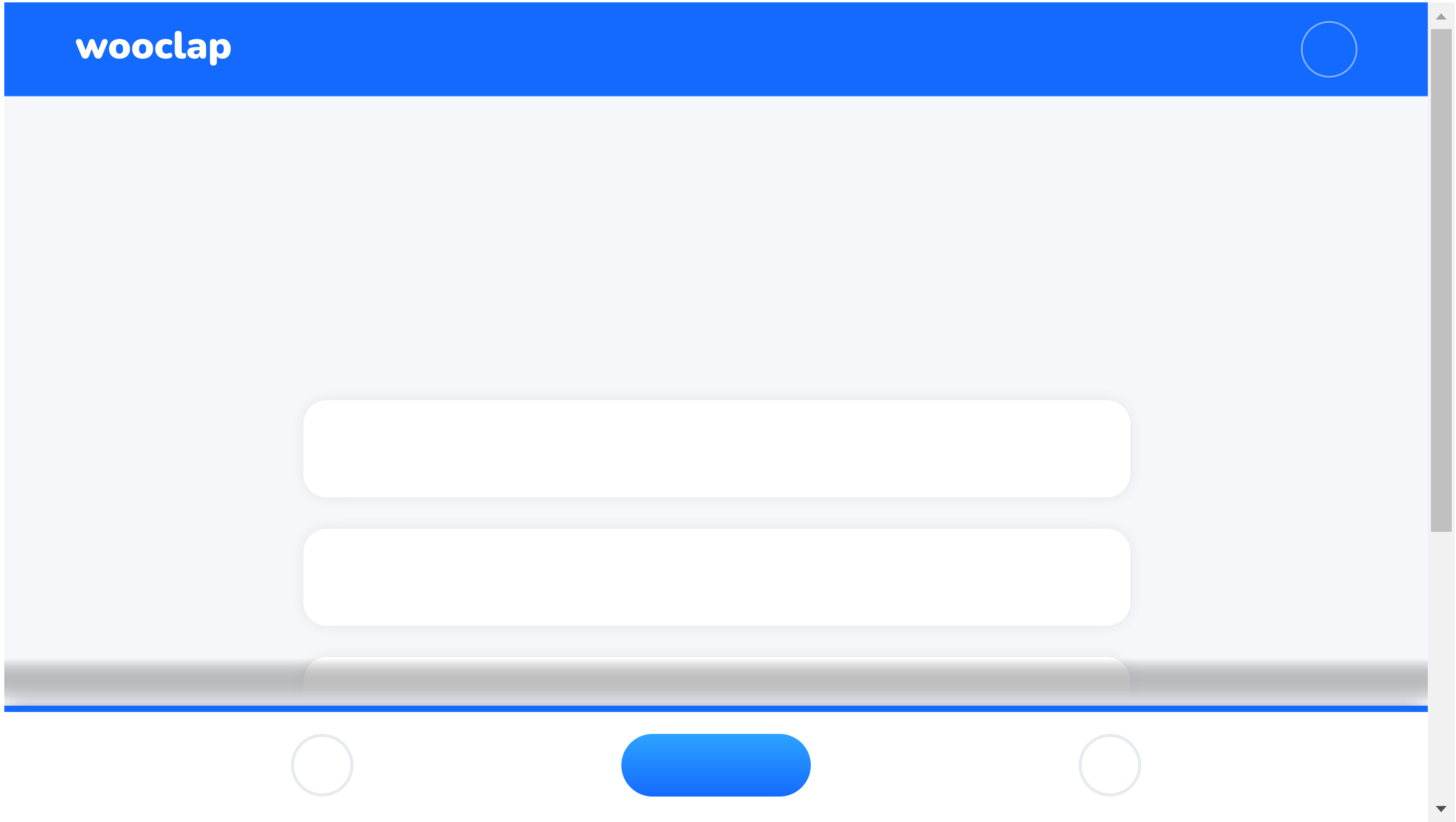
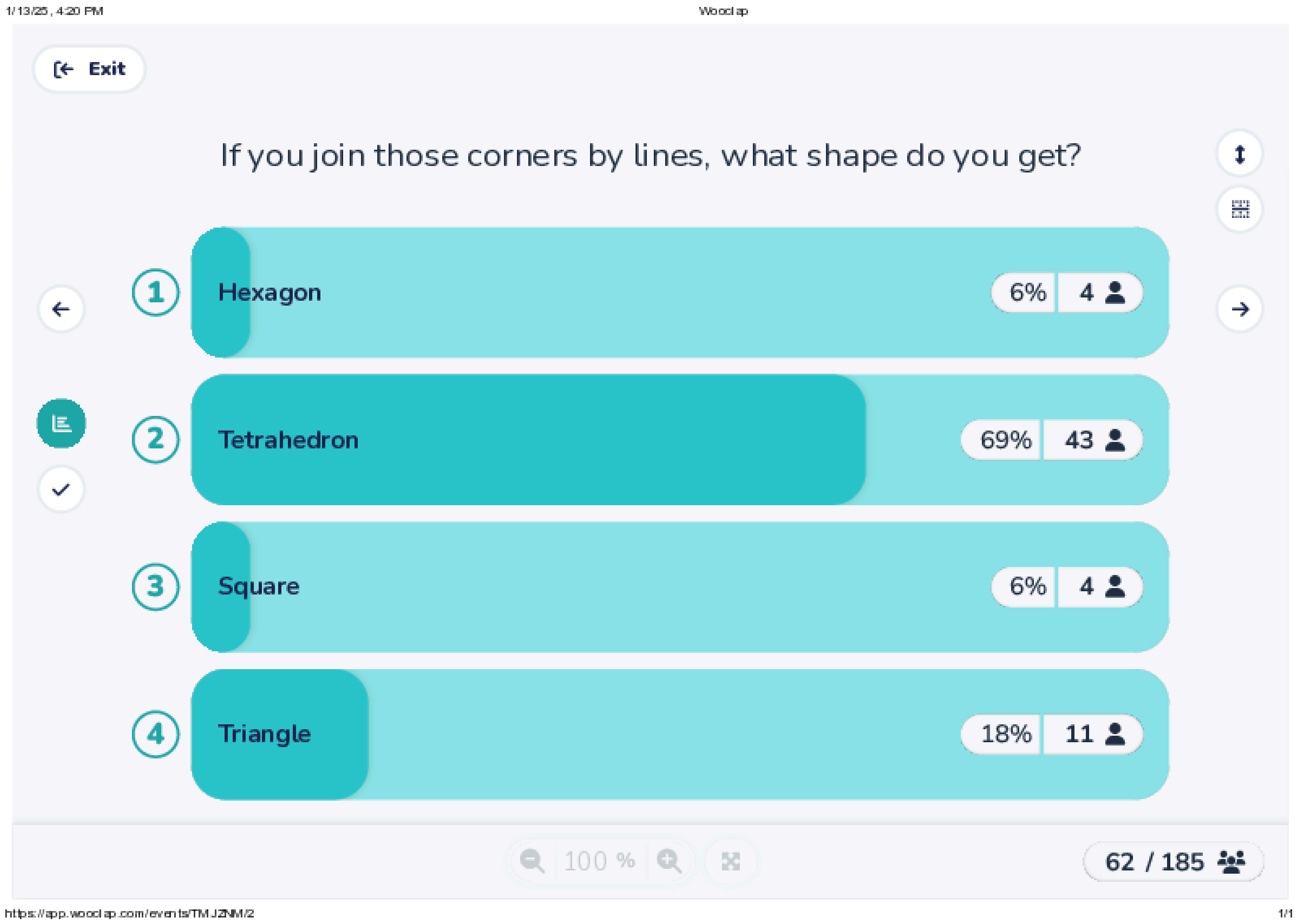
Let's get you thinking in 3D!

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



Results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If you join those corners by lines, what shape do you get?
1
Hexagon
6%
4
2
Tetrahedron
69%
43
3
Square
6%
4
4
Triangle
18%
11
100 %
62 / 185
https://app.wooclap.com/events/TMJZNM/2
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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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  - e.g. $\mathrm{Na^+Cl^-}$ and $\mathrm{Mg^{2+}SO_4^{2-}}$

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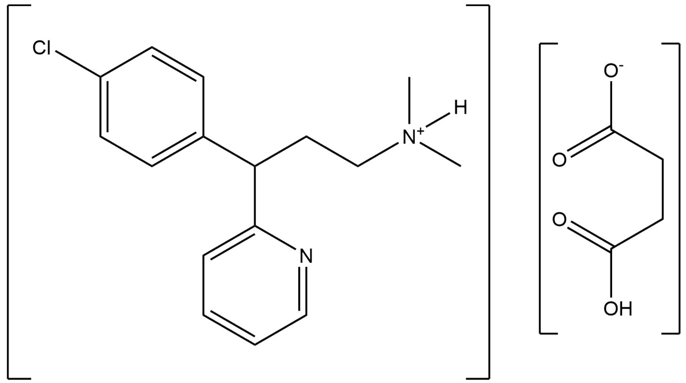
  - chlorphenirammonium maleate (active part of Piriton®)



Chlorphenirammonium maleate

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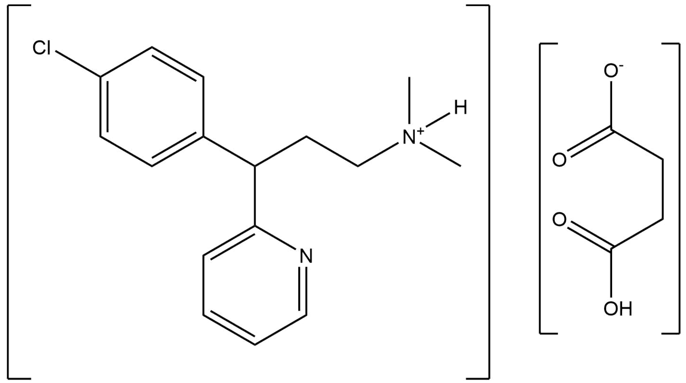
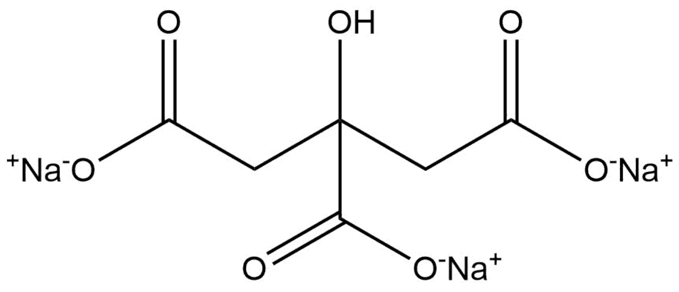
- (in)organic salts
  - Mono-/Di-/Tri-Sodium citrate $Na_xC_6H_{8-x}O_7$
    - collectively used as E331 in food
    - x can be varied from 1–3



Chlorphenirammonium maleate



Trisodium Citrate (x=3)

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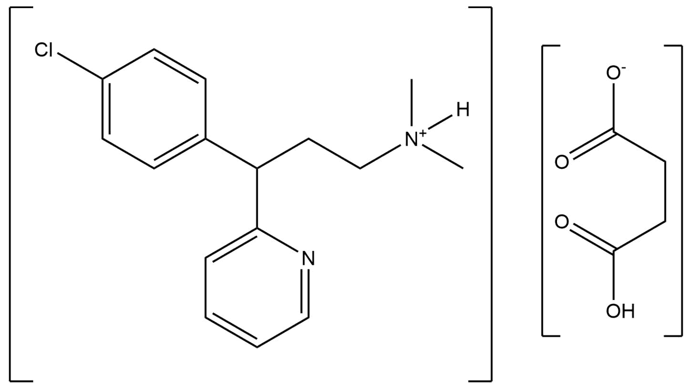
    - x can be varied from 1–3
- Ionic liquids
  - Either organic or inorganic, liquid below 100 °C



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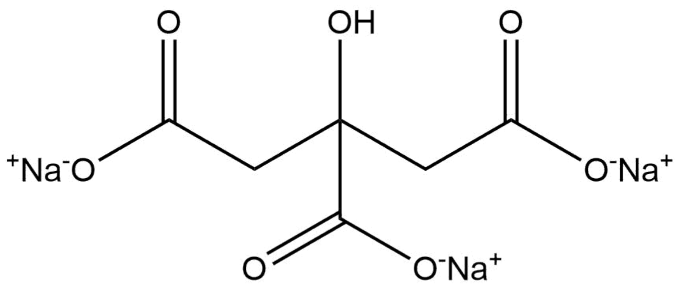

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Why are they interesting?

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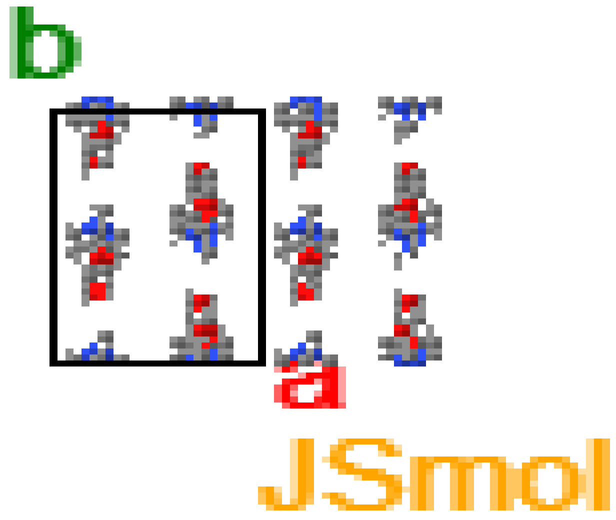
- High melting points due to Coloumbic energy (see later)
- Electrically insulating
  - Electronegativity differences promote localised electrons
- Usually hard, and often robust to harsh conditions
  - e.g. Synroc* is used to encapsulate nuclear waste

We can divide solids into two categories:

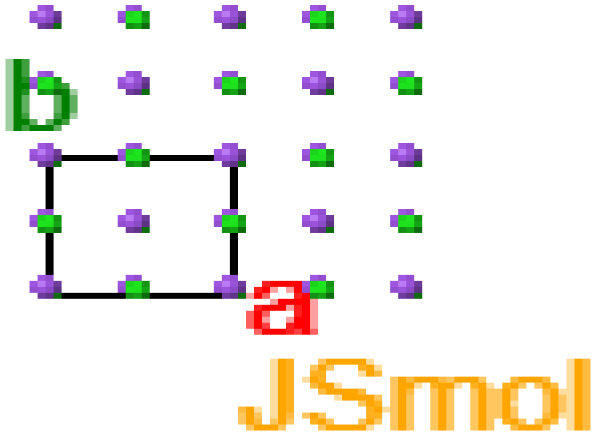
Molecular (e.g. paracetamol)

- Strong intramolecular bonds
- Weaker intermolecular interactions



Infinite (e.g. NaCl)

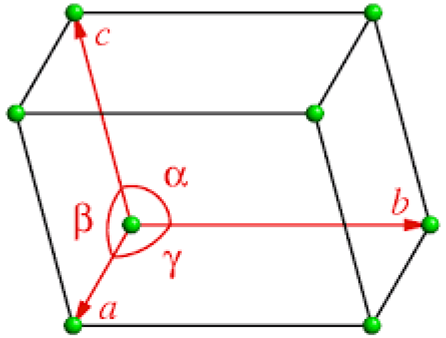
- Strong bonds between all atoms
- No discrete molecules



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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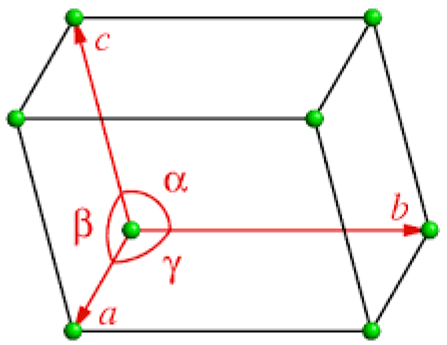

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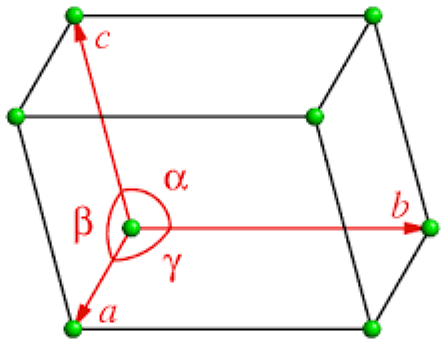
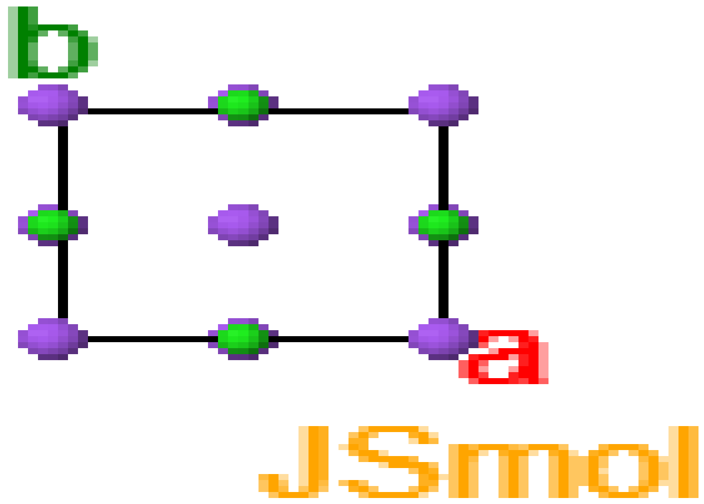


- Defined by lengths (a, b, c) and angles (α, β, γ)
  - 'Lattice parameters'
- Possesses 'space group' symmetry (an extension of point groups)
- Atom positions defined by fractional position along lattice directions

Example: Sodium chloride



Cubic structure	$a = b = c = 5.62$ Å, $\alpha = \beta = \gamma = 90°$				
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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  q is the charge on ions i, j and r is the distance between them
- $\frac{1}{r}$ dependence makes long-range interactions important

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

Infinite summations

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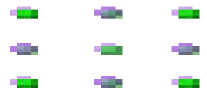
For example NaCl:

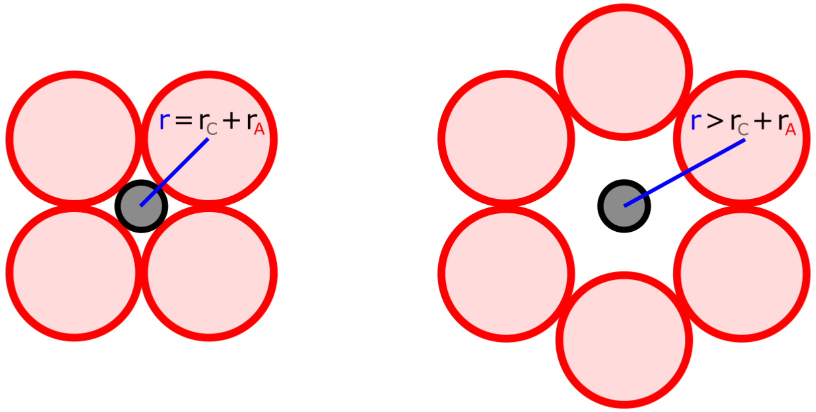


$$
\begin{aligned}
E_{\mathrm{Madelung}} &= \sum_{i \neq j} \frac{q_i q_j}{4\pi\epsilon_0 r} \\
&= \frac{\mathrm{N_A} q_i q_j}{4\pi\epsilon_0 r}\left(6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{2} + \frac{24}{\sqrt{5}} - \dots\right) \\
&\simeq \frac{\mathrm{N_A} q_i q_j}{4\pi\epsilon_0 r}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

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

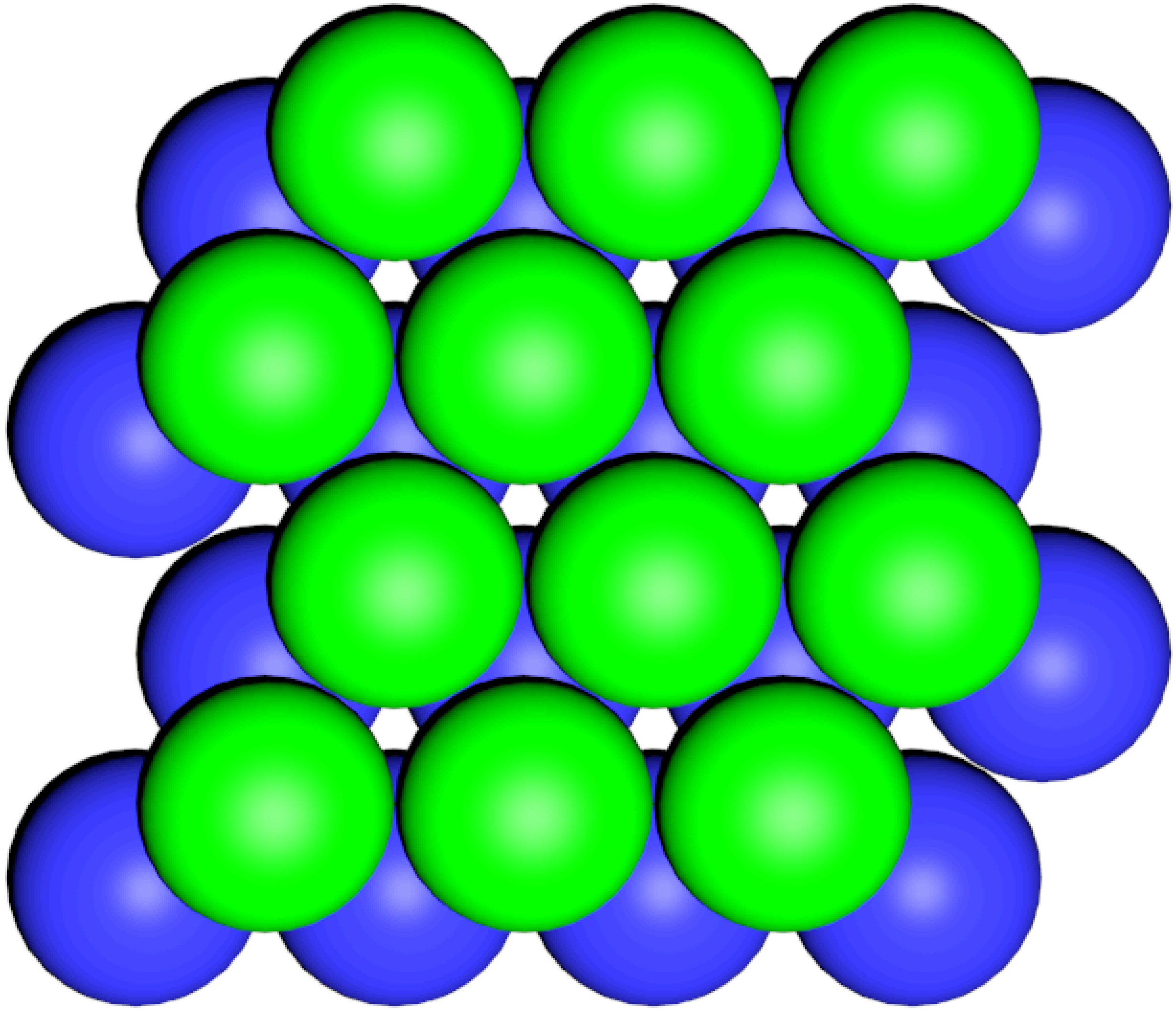


CN = 4
(6 in 3D)

CN = 6
(12 in 3D)

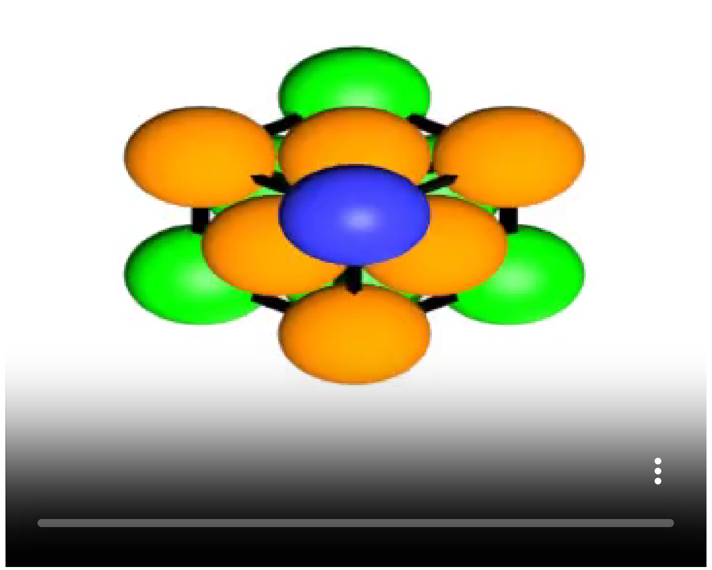
In many materials, the optimum is found when the largest ion (often oxide) is **close-packed**

Close packing

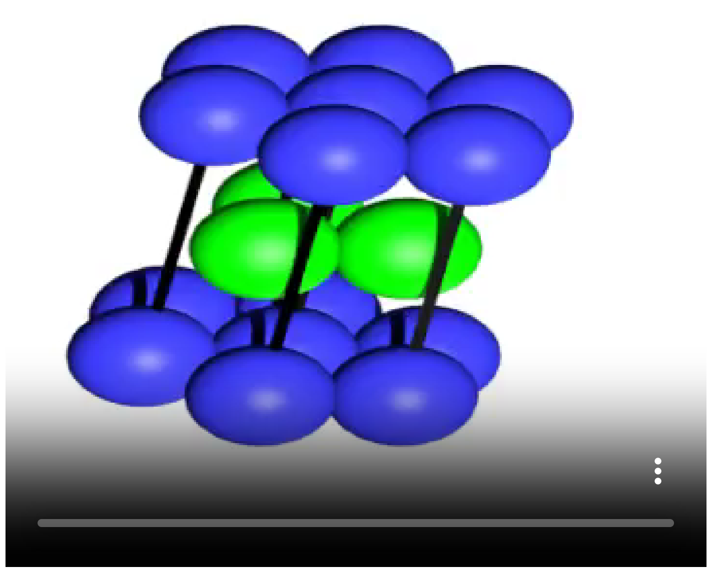


Close packing

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

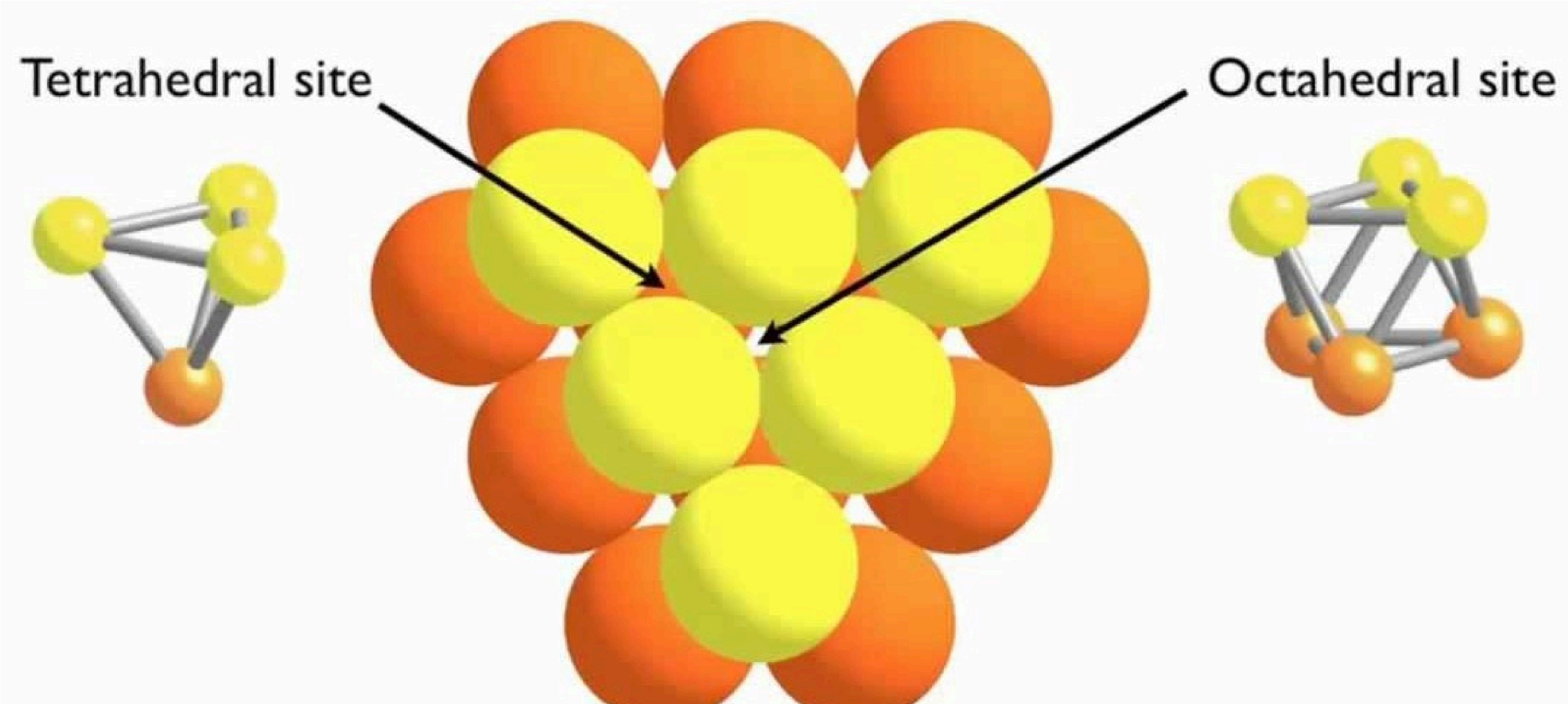


Hexagonal close-packed (HCP)
... ABABAB ...

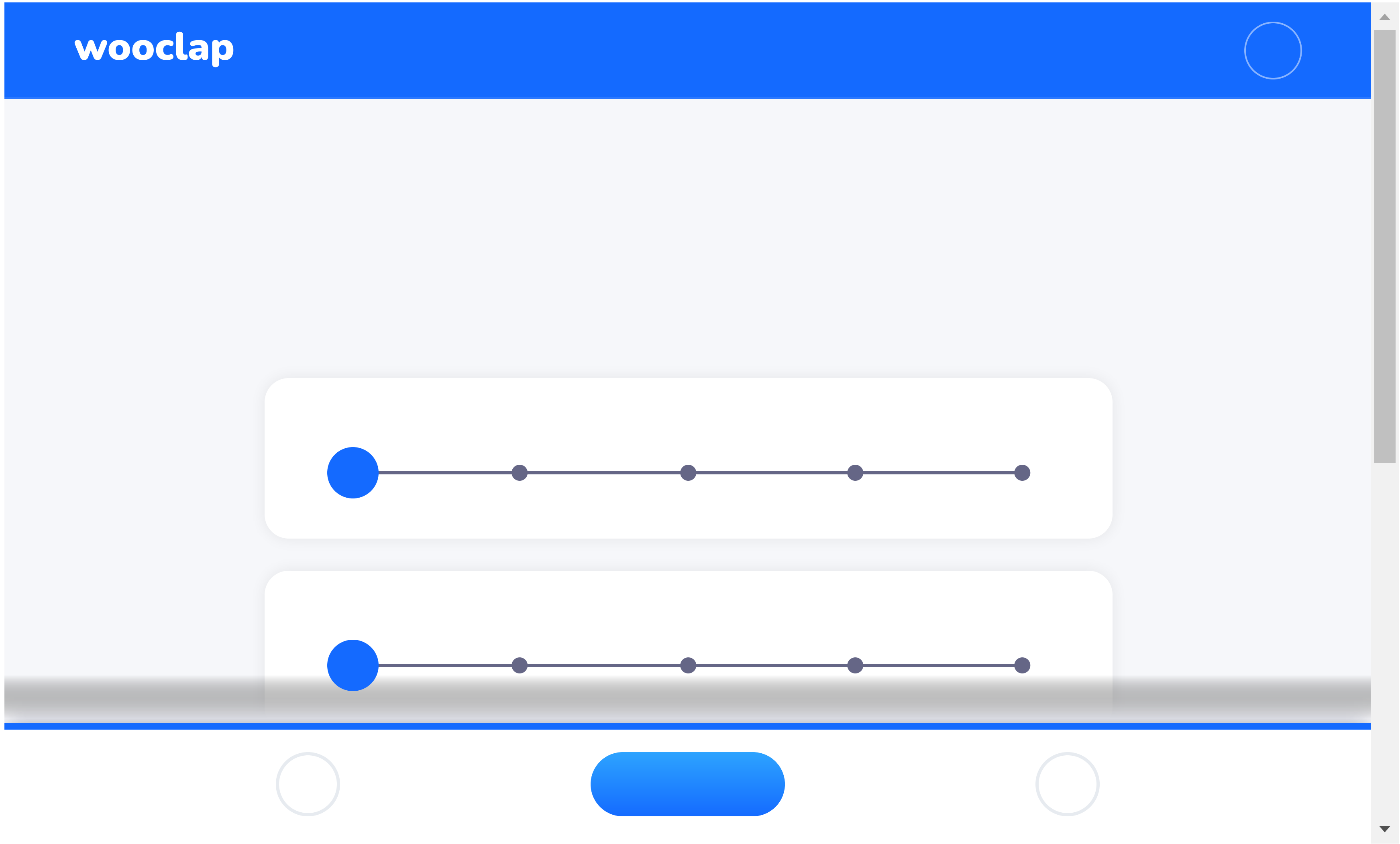


Holes

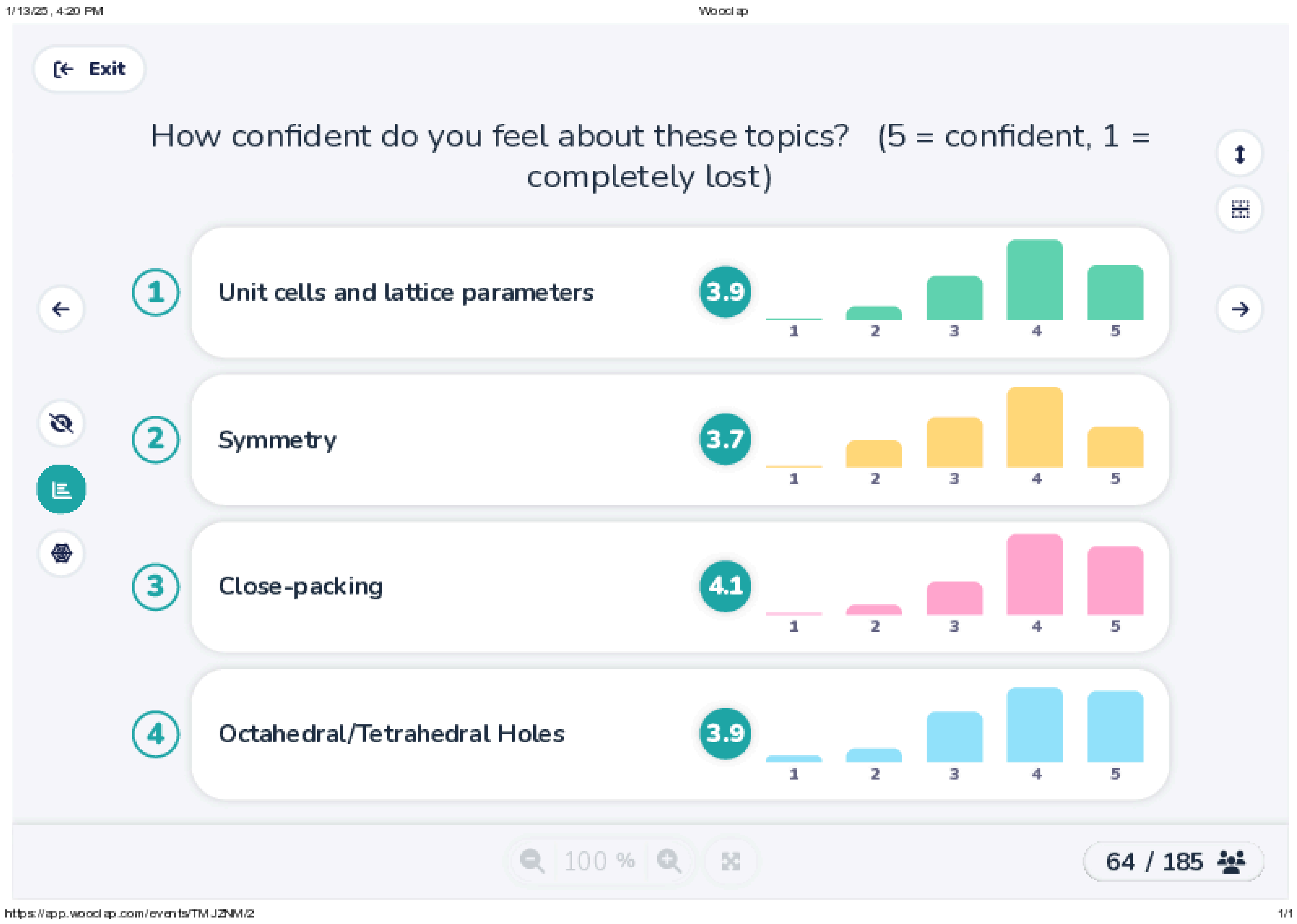
CP arrangements of large (an)ions [X] leave 'holes' within the structure, which can be occupied by smaller (cat)ions [M]



How are you getting on? Vote

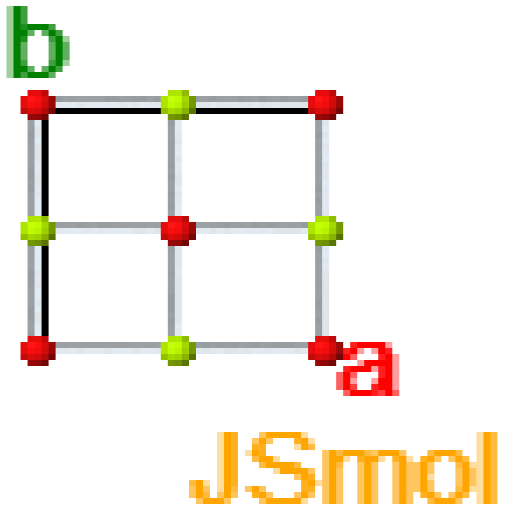


How are you getting on? Results

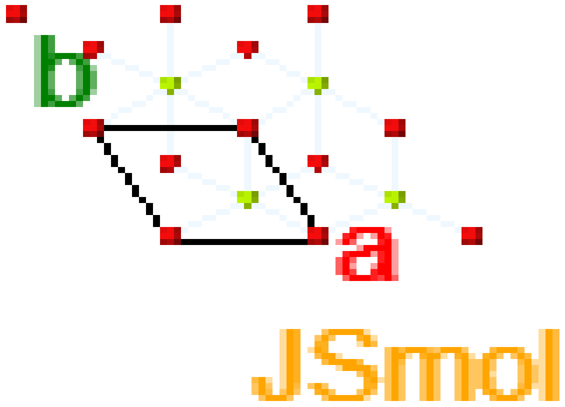


Octahedral holes

One hole per cp ion - both are 6-coordinate



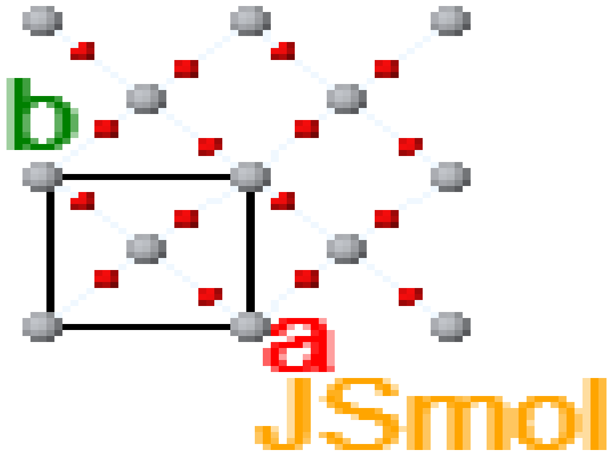
Rock salt (NaCl) structure



Nickel Arsenide structure (e.g. FeS)

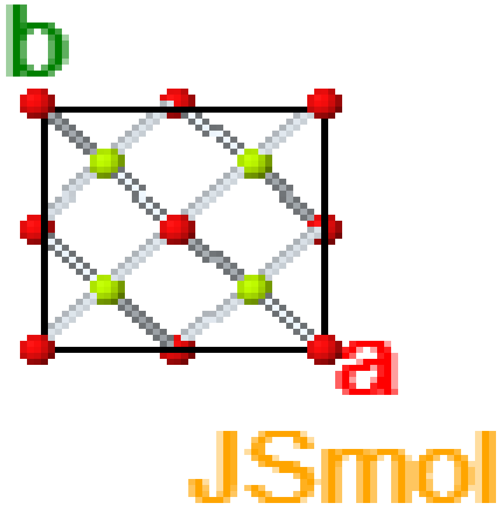
Rutile

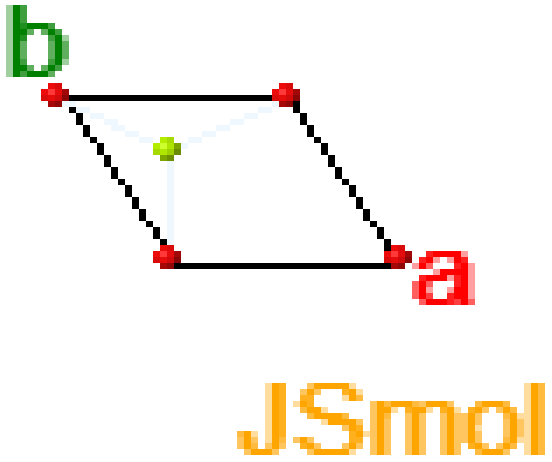
Although not strictly close-packed, rutile (TiO_2) is distorted HCP with Ti^{4+} filling half the octahedral holes CN = 6 / 3



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...)

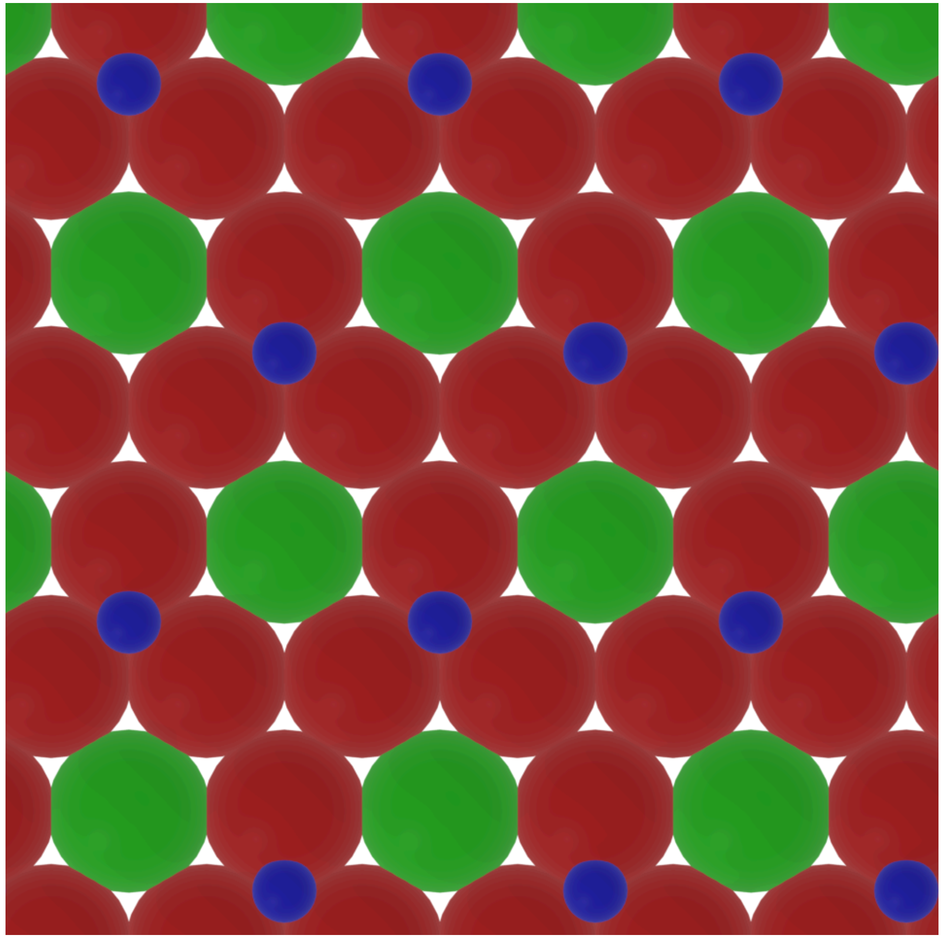
- Very difficult to predict!

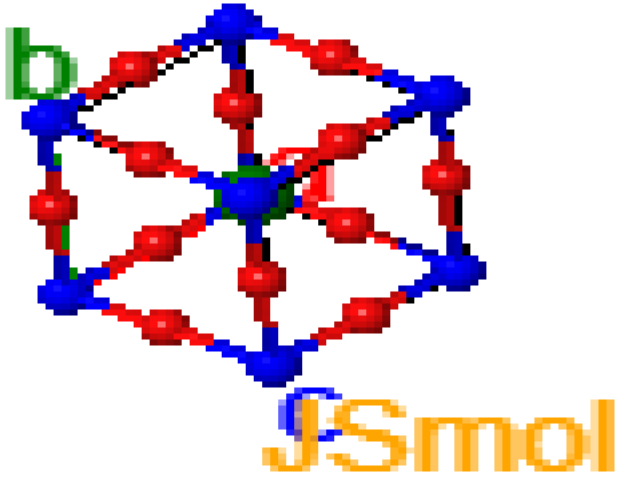
Beyond binary compounds

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