Descriptive Crystal Structures

Drawing/visualizing 3-dimensional structures can be very difficult—many 3-d crystal drawers/visualizers available online. 2-d representations take some practice and artistic skill.

Symmetry: previously we've worked with point groups

- rotational, reflection, inversion etc.
- defined by point, axis, or plane.

For extended structures (solids, crystals) we are interested in also looking at translational symmetry.

Consider NaCl:

1st layer: 

2nd layer: 

3rd layer: same as 1st

4th layer: same as 2nd

Identify repeating unit:

NaCl

we usually pick the one

Unit cell: can describe entire crystal structure by just translating by 1 unit cell at a time

no rotations or other symmetry operations to close pack unit cells (no voids)
In recognition of the unit cell, we can also draw them like this:

\[
\begin{align*}
  \text{O} &= \text{Na}: 0, 1 \\
  &\quad \text{Cl} : \frac{1}{2} \\
  \text{O} &= \text{Na}: \frac{1}{2} \\
  &\quad \text{Cl} : 0, 1
\end{align*}
\]

Specify \( z \) height \( \text{y/in unit cell length} \).

How to describe this structure more generally to group them with other similar structures?

**Lattice and Basis.**

- Na: 0
- Cl: 0

\[
\begin{align*}
\text{lattice } &\rightarrow \text{lattice } \rightarrow \\
\text{basis } &\rightarrow \text{O}
\end{align*}
\]

You can put the basis @ any point in the lattice to get the same structure (i.e., all lattice pts. are identical).

\[\Rightarrow \text{lattice: FCC (face-centered-cubic)}\]

**Basis:** Na \((0, 0, 0)\)
Cl \(\left(\frac{1}{2}, 0, 0\right)\)

\(\text{xyz, z y/in unit cell.}\)

Each unit cell should only contain 1 basis total (for primitive lattices).

\(\Rightarrow\) note: FCC is not a primitive lattice.

Total basis \( \geq 1 \).
Examples: CsCl

\[
\begin{array}{c}
\text{Cs} \\
\text{Cl}
\end{array}
\]

or

\[
\begin{array}{c}
\text{Cl} \\
\text{Cs}
\end{array}
\]

What is the lattice and basis? Not bcc!

Simple cubic, basis = Cs \((\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\) or could also be \(Cs(000)\)

\(Cl(000)\) for different unit cell drawing.

Simple cubic is primitive cell,

1 basis per unit cell.

To take note of edge sharing and vertex/face sharing

Each vertex shared amongst

8 unit cells.

Per unit cell: \(8 \times \frac{1}{8} = 1 \text{Cl} \)

\(\frac{2}{3}\) vertices sharing

\(+ \frac{1}{3} \text{Cl}\)

\(\frac{1}{2} \text{Cs}\)

\(1 \text{CsCl}\)
Example: Perovskites: $ABX_3$

\[ \text{cation diff.} \]
\[ \text{cation} \]

$\text{BaTiO}_3$

\[
\begin{align*}
O^+ &= O^+ (0,0,0) \\
\text{Ba} &= \text{Ba} (0,0,1) \\
\text{Ti} &= \text{Ti} (\frac{1}{2}) \\
O^- &= (0,0,1)
\end{align*}
\]

\[ \text{Ba} = \text{vertex} \]
\[ O = \text{face} \]
\[ \text{Ti} = \text{body} \]

Simple Cubic:

$\text{Ba} (0,0,0)$

$O (\frac{1}{2},0,0)$

$(0,\frac{1}{2},0)$

$(0,0,\frac{1}{2})$

$\text{Ti} (\frac{1}{2},\frac{1}{2},\frac{1}{2})$

Per unit cell: $\text{BaTiO}_3$.

Example: Silicon.

Each Si tetrahedrally coordinated.

Same structure as diamond.

FCC: Basic Si $(0,0,0)$

$(\frac{1}{4},\frac{1}{4},\frac{1}{4})$

Can think of it as one Si FCC lattice +

another Si FCC lattice offset by $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$.

See physical model, or use online 3-D visualizer.
We can also describe these structures based on hole filling.

Generally, two types of holes to fill:

4-coordinate tetrahedral

6-coordinate octahedral

Case I:
FCC Na structure, fill all the octahedral holes with Cl.

Case II:
FCC S\textsubscript{i} structure: fill $\frac{1}{2}$ of tetrahedral holes with S\textsubscript{i}. 