Kap. 5
Crystallography and crystal structures

Unit cell

Unit cell choices

LATTICE
BASIS / MOTIF

CRYSTAL STRUCTURE

Unit cell
Translation along x, y, z
Counting of atoms in 2D

- Atoms in a corner = $\frac{1}{4}$
- Atoms on an edge = $\frac{1}{2}$
- Atoms inside the cell = 1

\[ V = a \cdot (b \times c) \]
Counting of atoms in 3D

- A corner-atom is shared between 8 cells ⇒ $\frac{1}{8}$ atom pr. cell
- An edge-atom is shared between 4 cells ⇒ $\frac{1}{4}$ atom pr cell
- A surface-atom is shared between 2 cells ⇒ $\frac{1}{2}$ atom pr cell
- A atom inside one cell ⇒ 1 atom pr cell
Positioning of atoms

Can add and subtract whole numbers at will.

Crystal plane and crystal directions

A plane \((h\ k\ l)\)

A set of equivalent planes \(\{h\ k\ l\}\)

A direction \([h\ k\ l]\)

A set of equivalent directions \(<h\ k\ l>\)

The equivalent planes and directions are a result of the systems symmetry

e.g., fcc \(<111>\)

\([111] [\bar{1}11] [\bar{1}11] [1\bar{1}1]\)

\([\bar{1}11] [1\bar{1}1] [1\bar{1}1] [\bar{1}11]\)

Miller indices, 2D
### Directions

- **Plane A**
  - Intercept length: a, b, c
  - Reciprocal: \( \frac{1}{a}, \frac{1}{b}, \frac{1}{c} \)
  - Cleared fraction: 0, 2, 2, 0, 1
  - Miller indices: (102)

- **Plane B**
  - Intercept length: a, b, c
  - Reciprocal: \( \frac{1}{a}, \frac{1}{b}, \frac{1}{c} \)
  - Cleared fraction: 0, 2, 2, 0, 1
  - Miller indices: (201)

### Crystal plane and crystal directions

- **A plane**
  - \( (h \ k \ l) \)
- **A set of equivalent planes**
  - \( \{h \ k \ l\} \)
- **A direction**
  - \( [h \ k \ l] \)
- **A set of equivalent directions**
  - \( <h \ k \ l> \)

The equivalent planes and directions are a result of the system's symmetry:

- e.g. fcc \( <111> \)
  - \([111] \ [\bar{1}11] \ [\bar{1}1\bar{1}] \ [1\bar{1}1]\)
- \([\bar{1}1\bar{1}] \ [1\bar{1}1] \ [1\bar{1}\bar{1}] \ [\bar{1}11]\)

Parallel directions have the same index.
**Spherepacking**

The entities have to be:

- Spherical
- Of same type (size)
- Non-compressible
- Non-repulsive / contractive

![Ideal sphere packing model](image)

Any observed deviation from the ideal model will be explained by that the requirements are not fully met.

**Closest (densest) packing of spheres:**

- 74% of the volume is filled by the spheres
- 26% voids / vacant space

The voids/holes will have different appearance:

- Octahedral shape
- Tetrahedral shape
- (Trigonal prismatic holes)
- (Trigonal bipyramidale holes)

The voids/holes may be filled with atoms:

- of the same type as the packing spheres
- of different type
## Density of packing

<table>
<thead>
<tr>
<th>Coordination number (CN)</th>
<th>Name</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>Simple cubic</td>
<td>0.5236</td>
</tr>
<tr>
<td>8</td>
<td>Simple hexagonal</td>
<td>0.6046</td>
</tr>
<tr>
<td>8</td>
<td>Body-centred cubic</td>
<td>0.6802</td>
</tr>
<tr>
<td>10</td>
<td>Body-centred tetragonal</td>
<td>0.6981</td>
</tr>
<tr>
<td>12</td>
<td>Closest packing</td>
<td>0.7405</td>
</tr>
</tbody>
</table>

(a) An "open" packing  
(b) Close packing  
(c) Close packing
Dense sphere packing

hcp  
ccp

ABA  ABC

Cubique à faces centrées ABC  Hexagonal compact ABA

Octahedral sites  Tetrahedral sites  Holes

Tetrahedral  Octahedral
Tetraeder hole + Tetraeder hole - Octaeder hole

Octahedra holes
CN = 6

Tetrahedra holes
CN = 4

Hexagonal packing (AA..) Trigonal prismatic holes
CN = 6

Hexagonal closepacked (AB..) Trigonal bipyramidal
CN = 5

<table>
<thead>
<tr>
<th>Type of hole</th>
<th>Number</th>
<th>Max. radius</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cuboctahedron</td>
<td>N</td>
<td>1</td>
</tr>
<tr>
<td>Cube</td>
<td>N</td>
<td>0.732</td>
</tr>
<tr>
<td>Trigonal prismatic</td>
<td>2N</td>
<td>0.528</td>
</tr>
<tr>
<td>Octahedral</td>
<td>N</td>
<td>0.414</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>2N</td>
<td>0.225</td>
</tr>
<tr>
<td>Triangle</td>
<td>N</td>
<td>0.155</td>
</tr>
</tbody>
</table>
Diagonal = 4 \( r \),
Volume of cube = \( (2\sqrt{2} r)^3 \)
Volume of 4 spheres = \( 4\pi r^3 / 3 \)
Density = \( 16\pi / (2\sqrt{2})^3 = 0.7405 \)
\textbf{bcc, cubic, I-centered} \\
\((0,0,0) + (1/2,1/2,1/2)\) \\
\(\text{CN} = 8\)

\textbf{CsCl-type structure, CN = 8} \\
\(\text{M in (0,0,0)}\) \\
\(\text{X in (1/2,1/2,1/2)}\) \\
\(\text{Not I-centered, -> P}\)

\textbf{NaCl-type structure = cubic + basis} \\
\(\text{F-centered lattice:}\) \\
\(\text{Na in (0,0,0)}\) \\
\(\text{Cl in (1/2,0,0)}\)

\textbf{fcc, Cubic F-centered lattice} \\
\(\text{Structure = lattice + basis (motif)}\) \\
\(\text{F-centered lattice with metal in (0,0,0)}\)
hcp (hexagonal close packed)

\[ Z = 2 \]

2 atoms in unitcell:

\((0, 0, 0), (\frac{2}{3}, \frac{1}{3}, \frac{1}{2})\)

ccp (cubic close packed)

\[ Z = 4 \]

4 atoms in unitcell:

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

bcc

Body-Centred Cubic

\[ Z = 2 \]

2 atoms in unitcell:

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

Structure (types) derived from dense closepacking of spheres

Principe:

A. Closepacked layers of different types of spheres

B. Filling of holes with smaller spheres (octahedra-, tetrahedra-, trig. bipyramidal.- holes)

C. Combinations of \( A \) and \( B \)
**A**

\[ \text{TiAl}_3 \]

\[ \text{WAl}_5 = \text{WAl}_3 + \text{Al}_2 \]

---

**B**

**Filling of holes (interstitial positions)**

\[ \text{AB}_n \quad \text{M}_m \text{X} \]

\( X = \text{Packing sphere} \)

<table>
<thead>
<tr>
<th>Filling degree</th>
<th>( \text{AB}_n )</th>
<th>( \text{M}_m \text{X} )</th>
<th>Sphrepacking</th>
<th>hcp</th>
</tr>
</thead>
<tbody>
<tr>
<td>All octaederholes</td>
<td>AB</td>
<td>MX</td>
<td>NaCl</td>
<td>NiAs</td>
</tr>
<tr>
<td>All tetraederholes</td>
<td>AB</td>
<td>M</td>
<td>X</td>
<td>CaF₂</td>
</tr>
<tr>
<td>( \frac{1}{2} ) tetraederholes</td>
<td>AB</td>
<td>MX</td>
<td>ZnS(bl.)</td>
<td>ZnS(wu.)</td>
</tr>
<tr>
<td>( \frac{1}{2} ) octaederholes</td>
<td>AB</td>
<td>M( \frac{1}{2} )</td>
<td>X</td>
<td>CdCl₂</td>
</tr>
<tr>
<td>( \frac{1}{3} ) octaerholes</td>
<td>AB</td>
<td>M( \frac{1}{3} )</td>
<td>X</td>
<td>CrCl₃</td>
</tr>
</tbody>
</table>

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**C**

**Mixed spheres in dense packed layers + filling of interstitial holes**

A, B --- cations  
X --- anion

A and X of similar size  
B is so small that it fits into octaeder holes

**AX₃** densepacked layers

Those octahedra holes with 6 neighbours of X type is filled with B

**ABX₃** perovskite type structure
Perovskite

Space group: Pm-3m (No. 221)

High symmetry
Large Mandelung constant
Large crystal energy

Enables costly electron configurations

Interesting properties
**Perovskite**

<table>
<thead>
<tr>
<th>Property</th>
<th>Compound examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Insulator</td>
<td>LaGaO₃, LaAlO₃, LaCrO₃, LaFeO₃</td>
</tr>
<tr>
<td>High-K dielectric</td>
<td>BaTiO₃, Ba₂EuZrO₅, Ca₂Cu₃Ti₄O₁₂</td>
</tr>
<tr>
<td>Semi-conductivity</td>
<td>LaMnO₃, PbCrO₃, RTiO₃ (R = La...Tm)</td>
</tr>
<tr>
<td>Half metallicity</td>
<td>LaBaMn₂O₆.₅, YBaMn₂O₆.₅, Sr₂FeMoO₆, Ba₂FeMoO₆, Ca₂FeMoO₆, Ca₂FeReO₆</td>
</tr>
<tr>
<td>Metallic conductivity</td>
<td>LaNiO₃</td>
</tr>
<tr>
<td>Superconductivity</td>
<td>YBa₂Cu₃O₇, HgBa₂Cu₃O₇, La₁₋ₓNdₓCaBa₂Cu₃O₇,</td>
</tr>
<tr>
<td></td>
<td>Bi₂Sr₂Ca₂Cu₃O₁₀₋ₓ, HgBa₂Ca₂Cu₃O₁₁₋ₓ</td>
</tr>
<tr>
<td>Colossal magnetoresistance</td>
<td>AₓLa₀.₇MnO₃ (A = Ca, Sr, Pr, Pb)</td>
</tr>
<tr>
<td>Multi ferroics</td>
<td>BiMnO₃, BiFeO₃</td>
</tr>
<tr>
<td>Ferroelectricity</td>
<td>LaCoO₃</td>
</tr>
<tr>
<td>Ferromagnetic</td>
<td>SrRuO₃, LaMnO₃,La₁₋ₓCaₓMnO₃, Sr₁₋ₓLaMnO₃</td>
</tr>
<tr>
<td>Anti ferro</td>
<td>BiMnO₃, LaFeO₃, LaMnO₃</td>
</tr>
<tr>
<td>Piezoelectricity</td>
<td>PbZr₀.₄₇Ti₀.₅₃O₃</td>
</tr>
<tr>
<td>Spin glass</td>
<td>CaRuO₃</td>
</tr>
<tr>
<td>Multi valence materials</td>
<td>Ca₂Co₂O₆, Sr₂Fe₄O₁₁, YBaMn₂O₆.₅</td>
</tr>
</tbody>
</table>

**Space filling of polyhedra**

Structures can be described as connections of polyhedra that share:

- Corners
- Edges
- Faces

The polyhedra are simplified for visual clarity.

**Type of polyhedra:**

- Tetrahedra
- Octahedra
- Trigonal prismatic

Basically the same types of polyhedra as mention for sphere packing.

**Limited units, Octahedra**

- Isolated octahedra: MX₆
- Dimer: M₂X₁₁ (Nb₂F₁₁⁻)
- Dimer: M₂X₁₀ (Nb₂Cl₁₀) (U₂Cl₁₀)
- Dimer: M₂X₉ (Fe₃(CO)₉) (I₂O₉⁴⁻)

**Octahedra**

Connected by:
- Corners
- Edges
- (Faces)

**Tetrahedra**

Connected by:
- Corners

How these units connect will affect the chemical composition, and vice versa.
Polymerization of MX₆ octahedra

Corner sharing:
\[ d(M-M) = 2 \times d(M-X) \]

Edge sharing:
\[ d(M-M) = \sqrt{2} \times d(M-X) \]

Face sharing:
\[ d(M-M) = 1.16 \times d(M-X) \]

Infinite systems; octahedra by corner sharing

Number of corners shared in a given octahedra:
2, (3), 4, (5), 6

AX₅ chains: (cis-, trans-)
- cis- VF₅
- trans- BiF₅

AX₄ layers:
- SnF₄
- K₂NiF₄

AX₃ 3D network:
- ReO₃
- FeF₃
- ABX₃ perovskite
Structures based on tetrahedras

<table>
<thead>
<tr>
<th>No.</th>
<th>Vertices shared</th>
<th>Formula</th>
<th>Type of complex</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A_2X_4</td>
<td>Finite molecule or pyro ion</td>
<td>Cl_2O_7, S_2O_5_2−, etc.</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>(AX)_3</td>
<td>Cyclic molecule, or meta-ion</td>
<td>S_2O_4, Se_2O_4, (PCl_2)_n (P_2O_5)_4, (SiO_2)_6, (SO_3)_3, (PO_3)_n</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>(A_2X_5)_n</td>
<td>Infinite chain</td>
<td>P_4O_10, Al[AlSiO_3], P_2O_5, Li_2Si_2O_5, P_2O_5, La_2[Be_2O_5]</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>(AX)_2</td>
<td>Layer, double layer, or 3D structure</td>
<td>Hgl_2 (red), CaSi_2Al_2O_8 (hexag.), SiO_2 structures, Ge_2</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>(AX)_3</td>
<td>Infinite layer</td>
<td>AlOCl, GaOCl</td>
<td></td>
</tr>
</tbody>
</table>

Structures based on tetrahedras

<table>
<thead>
<tr>
<th>No.</th>
<th>Vertices shared</th>
<th>Formula</th>
<th>Type of complex</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A_2X_6</td>
<td>Finite dimer</td>
<td>Al_2Cl_6, Fe_2Cl_6</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>(AX)_2</td>
<td>Infinite chain</td>
<td>BeCl_2, SiS_2, Be(CH_3)_2</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>(A_2X_3)_n</td>
<td>Infinite double chain</td>
<td>Cs(Cu_2Cl_3)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>(AX)_n</td>
<td>Infinite layer</td>
<td>LiOH, PbO</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>(A_2X)_n</td>
<td>3D structures</td>
<td>Li_2O, F_2Ca</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>(AX)_n</td>
<td>Double layer</td>
<td>La_2O_3, Ce_2O_2S, U_2N_2Sb</td>
<td></td>
</tr>
</tbody>
</table>

Polymerization of MX_4 tetrahedra

- **Corner sharing:**
  \[ d(M-M) = 2d(M-X) \]
  2.0 only observed for SiO_4
  Si^{4+} - Si^{4+} repulsions

- **Edge sharing:**
  \[ d(M-M) = 1.16d(M-X) \]

- **Face sharing:**
  \[ d(M-M) = 0.67d(M-X) \]
CaF$_2$
FCa$_4$ - tetraheda

Na$_2$O
NaO$_4$ - tetraheda

Sink blende
ZnS$_4$, S$_2$Zn$_4$

Wurtzit
ZnS$_4$, S$_2$Zn$_4$

Silicates:

SiO$_4$ tetrahedas
Corner (vertex) sharing, never edge or face (too strong Si$^{4+}$-Si$^{4+}$ repulsions)
Only two SiO$_4$ tetrahedra share a common corner

Bridging oxygens count $\frac{1}{2}$
Non-bridging count 1

$A_2X_{11}$

$A_3X_3$

$A_2X_5$

$A_6X_{17}$

Rings 1:3
Double rings 1:2.5
Layer 1:2.5
Double layer ... 1:2
3D 1:2
### Relation between chemical formula and silicate anion structure

<table>
<thead>
<tr>
<th>Si:O ratio</th>
<th>Number of oxygens per Si</th>
<th>Type of silicate anion</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:4</td>
<td>0</td>
<td>isolated $\text{SiO}_4^{4-}$</td>
<td>Mg$_2$SiO$_4$ olivine, Li$_2$SiO$_3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>dimer $\text{Si}_2\text{O}_5^{6-}$</td>
<td>Ca$_2$Si$_2$O$_7$, rankinite, Sc$_2$Si$_2$O$_7$, thortveite</td>
</tr>
<tr>
<td>1:3</td>
<td>2</td>
<td>chains ($\text{SiO}_3$)$_2^{6-}$</td>
<td>Na$_2$SiO$_3$, MgSiO$_3$ pyroxene</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>rings, eg $\text{Si}_3\text{O}_5^{6-}$</td>
<td>CaSiO$_3$, BaTiSi$_3$O$_9$, benitoite</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>$\text{Si}_2\text{O}_5^{6-}$</td>
<td>Be$_2$Al$_2$Si$_2$O$_8$, beryl</td>
</tr>
<tr>
<td>1:2:5</td>
<td>3</td>
<td>infinite sheets ($\text{Si}_2\text{O}_5^{6-}$)</td>
<td>Na$_2$Si$_3$O$_8$</td>
</tr>
<tr>
<td>1:2</td>
<td>4</td>
<td>3D framework $\text{SiO}_4^{4-}$</td>
<td>Si$_2\text{O}_5^{6-}$</td>
</tr>
</tbody>
</table>

*CaSiO$_3$ is dimorphic. One polymorph has $\text{Si}_2\text{O}_5^{6-}$ rings. The other polymorph has infinite ($\text{SiO}_3$)$_2^{6-}$ chains.

$^1$The three main polymorphs of silica, quartz, tridymite and cristobalite each have a different kind of 3D framework structure.