CRYSTAL CHEMISTRY

What is crystal chemistry?

- description and classification of crystals
- bonding; composition-structure relationships
- the conditions in which particular type of crystal structure is observed
- structure-property relations

Common ways to describe crystals:

- unit cell approach (specify size, shape and atomic positions)
- close-packing approach (good for metals, alloys, ionic structures, covalent networks, molecular and supramolecular solids)
- space-filling polyhedron approach

Reading:
New West Ch. 1 & 3
CLOSE-PACKED CRYSTAL STRUCTURES

Consider the close-packing of incompressible (hard) spheres:

In 2D, regular close-packing requires an hexagonal array (HCP)

Most efficient way to pack spheres of single size
• 6 nearest neighbors

Coordination number (CN): 6

In 3D, regular close-packing involves stacking 2D HCP arrays

Regular (crystalline) packing

Irregular packing
HEXAGONAL CLOSE-PACKED STRUCTURE

An HCP crystal is a close-packed structure with the stacking sequence ...ABABAB...

To construct:
1\textsuperscript{st} layer: 2D HCP array (layer A)
2\textsuperscript{nd} layer: HCP layer with each sphere placed in alternate interstices in 1\textsuperscript{st} layer (B)
3\textsuperscript{rd} layer: HCP layer positioned directly above 1\textsuperscript{st} layer (repeat of layer A)

...ABABABAB...

HCP is two interpenetrating simple hexagonal lattices displaced by $a_1/3 + a_2/3 + a_3/2$
HCP STRUCTURE

- not a Bravais lattice

Orientation alternates with each layer

- each sphere touches 12 equidistant nearest neighbors (CN = 12)

Six in plane, six out-of-plane

- structure has maximum packing fraction possible for single-sized spheres (0.74)
HCP STRUCTURE

- Ideal ratio $c/a$ of $\sqrt{8/3} = 1.633$
- $\{0002\}$ planes are close packed
- Ranks in importance with FCC and BCC Bravais lattices

Unit cell is a simple hexagonal lattice with a two-point basis

Plan view
HCP STRUCTURE

- about 30 elements crystallize in the HCP form

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>( a ) (Å)</th>
<th>( c )</th>
<th>( c/a )</th>
<th>ELEMENT</th>
<th>( a ) (Å)</th>
<th>( c )</th>
<th>( c/a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>2.29</td>
<td>3.58</td>
<td>1.56</td>
<td>Os</td>
<td>2.74</td>
<td>4.32</td>
<td>1.58</td>
</tr>
<tr>
<td>Cd</td>
<td>2.98</td>
<td>5.62</td>
<td>1.89</td>
<td>Pr</td>
<td>3.67</td>
<td>5.92</td>
<td>1.61</td>
</tr>
<tr>
<td>Ce</td>
<td>3.65</td>
<td>5.96</td>
<td>1.63</td>
<td>Re</td>
<td>2.76</td>
<td>4.46</td>
<td>1.62</td>
</tr>
<tr>
<td>α-Co</td>
<td>2.51</td>
<td>4.07</td>
<td>1.62</td>
<td>Ru</td>
<td>2.70</td>
<td>4.28</td>
<td>1.59</td>
</tr>
<tr>
<td>Dy</td>
<td>3.59</td>
<td>5.65</td>
<td>1.57</td>
<td>Sc</td>
<td>3.31</td>
<td>5.27</td>
<td>1.59</td>
</tr>
<tr>
<td>Er</td>
<td>3.56</td>
<td>5.59</td>
<td>1.57</td>
<td>Tb</td>
<td>3.60</td>
<td>5.69</td>
<td>1.58</td>
</tr>
<tr>
<td>Gd</td>
<td>3.64</td>
<td>5.78</td>
<td>1.59</td>
<td>Ti</td>
<td>2.95</td>
<td>4.69</td>
<td>1.59</td>
</tr>
<tr>
<td>He (2 K)</td>
<td>3.57</td>
<td>5.83</td>
<td>1.63</td>
<td>Tl</td>
<td>3.46</td>
<td>5.53</td>
<td>1.60</td>
</tr>
<tr>
<td>Hf</td>
<td>3.20</td>
<td>5.06</td>
<td>1.58</td>
<td>Tm</td>
<td>3.54</td>
<td>5.55</td>
<td>1.57</td>
</tr>
<tr>
<td>Ho</td>
<td>3.58</td>
<td>5.62</td>
<td>1.57</td>
<td>Y</td>
<td>3.65</td>
<td>5.73</td>
<td>1.57</td>
</tr>
<tr>
<td>La</td>
<td>3.75</td>
<td>6.07</td>
<td>1.62</td>
<td>Zn</td>
<td>2.66</td>
<td>4.95</td>
<td>1.86</td>
</tr>
<tr>
<td>Lu</td>
<td>3.50</td>
<td>5.55</td>
<td>1.59</td>
<td>Zr</td>
<td>3.23</td>
<td>5.15</td>
<td>1.59</td>
</tr>
<tr>
<td>Mg</td>
<td>3.21</td>
<td>5.21</td>
<td>1.62</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nd</td>
<td>3.66</td>
<td>5.90</td>
<td>1.61</td>
<td>“Ideal”</td>
<td></td>
<td></td>
<td>1.63</td>
</tr>
</tbody>
</table>
A CCP crystal is a close-packed structure with the stacking sequence ...ABCABC...

To construct:
1st layer: 2D HCP array (layer A)
2nd layer: HCP layer with each sphere placed in alternate interstices in 1st layer (B)
3rd layer: HCP layer placed in the other set of interstitial depressions (squares, C)
4th layer: repeats the 1st layer (A)

It turns out that the CCP structure is just the FCC Bravais lattice!
CCP STRUCTURE

- CN = 12, packing fraction 0.74
- \{111\} planes are close packed
- 4 atoms in unit cell

Plan view
CLOSE-PACKED STRUCTURES

• most common are HCP and CCP

• an infinite # of alternative stacking sequences exist

Example: silicon carbide has over 250 polytypes
e.g., 6H-SiC
stacking sequence …ABCACB…
Stacking faults are one or two layer interruptions in the stacking sequence that destroy lattice periodicity.

The stacking fault is an example of a planar defect:

- stacking fault energy $\gamma \sim 100 \text{ mJ m}^{-2}$
- also results in a linear defect called a dislocation
EXAMPLE

InAs nanowires - <110> projection

• CCP and HCP have very similar lattice energies
• no clear cut trends
Rare Gases: Ne, He, Ar, Kr, Xe (CCP)
gold nanocrystals
X. M. Lin
ANOTHER VIEW OF CLOSE PACKING

(a) Hexagonal Close Packing
Mg, Be, Sc, Ti...

(b) Cubic Close Packing
Cu, Ca, Sr, Ag, Au, ...

hcp

ccp/fcc
Close Packing of Spheres

The most efficient way to fill space with spheres

Is there another way of packing spheres that is more space-efficient?

In 1611 Kepler asserted that there was no way of packing equivalent spheres at a greater density than that of a face-centred cubic arrangement. This is now known as the Kepler Conjecture.

This assertion has long remained without rigorous proof. In 1998 Hales announced a computer-based solution. This proof is contained in over 250 manuscript pages and relies on over 3 gigabytes of computer files. It was reviewed by a panel of 12 referees; the panel reported in 2003, after 4 years of work, that it was “99% certain” of the correctness of the proof, but couldn’t verify all of the computer calculations. Hales and Ferguson (his student) received the Fulkerson Prize for outstanding papers in the area of discrete mathematics in 2009.

In 2003, Hales announced that he would pursue a formal proof of the Conjecture that could be verified by computer. He estimated that the proof would be finished by 2023…but it was announced complete on Aug 10, 2014!!!!

In January 2015 Hales and 21 collaborators published "A formal proof of the Kepler conjecture". The proof was accepted in 2017.

http://en.wikipedia.org/wiki/Kepler_conjecture
PACKING FRACTIONS

The fraction of the total crystal volume that is occupied by spheres

CCP (and HCP)

radius = \( \frac{a\sqrt{2}}{4} \)

\[
\text{fraction} = \frac{V_{\text{atoms}}}{V_{\text{cell}}} = \frac{4 \times \frac{4}{3} \pi \left(\frac{a\sqrt{2}}{4}\right)^3}{a^3} = \frac{\pi}{6} \sqrt{2} = 0.7405
\]

74%

BCC

radius = \( \frac{a\sqrt{3}}{4} \)

\[
\text{fraction} = \frac{2 \times \frac{4}{3} \pi \left(\frac{a\sqrt{3}}{4}\right)^3}{a^3} = 0.6802
\]

68%

SC

\[
\text{fraction} = \frac{\frac{4}{3} \pi \left(\frac{a}{2}\right)^3}{a^3} = 0.5236
\]

52%
Close Packing of Spheres

Comparison of Packing Efficiencies

Primitive Cubic [α-Po]
Coordination Number 6
52% Packing Efficiency

\[ \frac{V_{\text{atoms}}}{V_{\text{cell}}} = 0.52, \text{ since} \]
\[ V_{\text{cell}} = a^3 \text{ and} \]
\[ V_{\text{atoms}} = Z \frac{4}{3} \pi r^3 \]
with \( a = 2r \) and \( Z = 1 \)

Body-Centered Cubic [W]
Coordination Number 8
68% Packing Efficiency

Close-Packed (ccp or hcp)
Coordination Number 12
74% Packing Efficiency

(increased pressure favors higher packing efficiency)
DENSITY CALCULATION

\[ \rho = \frac{m_{\text{atoms}}}{V_{\text{cell}}} = \left( \frac{nA}{N_A} \right) \frac{1}{V_C} \]

- \( n \): number of atoms/unit cell
- \( A \): atomic mass
- \( V_C \): volume of the unit cell
- \( N_A \): Avogadro’s number
  
  \((6.023 \times 10^{23} \text{ atoms/mole})\)

Calculate the density of copper.

\( R_{\text{Cu}} = 0.128 \text{ nm} \), Crystal structure: FCC, \( A_{\text{Cu}} = 63.5 \text{ g/mole} \)

\( n = 4 \text{ atoms/cell} \), \( V_C = a^3 = (2\sqrt{2}R)^3 = 16\sqrt{2}R^3 \)

\[ \rho = \frac{(4)(63.5)}{[16\sqrt{2}(1.28 \times 10^{-8})^3 \times (6.023 \times 10^{23})]} = 8.89 \text{ g/cm}^3 \]

8.96 g/cm\(^3\) in the literature
A large number of ionic structures can be regarded as built of CP layers of anions with the cations placed in interstitial sites.

For every anion, there is 1 Octahedral site and 2 Tetrahedral sites.

Fig. 7.7 Interstitial sites in a c.p. structure. Heavy circles are above and the dashed circles below the plane of the paper: (a) T⁺ site, (b) T⁻ site, (c) O site.
Octahedral holes

coordinates:
½00
0½0
00½
½1½
½1½
cavities have <100> orientation

+ = O site
Tetrahedral holes in CCP

**T⁺ sites:**
- $\frac{3}{4}\frac{1}{4}\frac{1}{4}$
- $\frac{1}{4}\frac{3}{4}\frac{1}{4}$
- $\frac{1}{4}\frac{1}{4}\frac{3}{4}$
- $\frac{3}{4}\frac{3}{4}\frac{3}{4}$

**T⁻ sites:**
- $\frac{1}{4}\frac{1}{4}\frac{1}{4}$
- $\frac{3}{4}\frac{3}{4}\frac{1}{4}$
- $\frac{1}{4}\frac{3}{4}\frac{3}{4}$
- $\frac{3}{4}\frac{1}{4}\frac{3}{4}$

cavities have <111> orientation
Holes in HCP

O sites: 
2/3, 1/3, 1/4
2/3, 1/3, 3/4

T+ sites: 
1/3, 2/3, 1/8
0, 0, 5/8

T− sites: 
0, 0, 3/8
1/3, 2/3, 7/8
LOCATION OF OCTAHEDRAL HOLES

**CCP**

Location of OCTAHEDRAL Interstitial Holes

1 per sphere

**HCP**

$1/4, 3/4$
LOCATION OF TETRAHEDRAL HOLES

(3/8 of a unit cell directly above/below each anion)
SIZE OF OCTAHEDRAL CAVITY

Only cations smaller than the diameter of the cavity can fit without forcing the anion lattice to expand.

\[ M = \text{cation} \]
\[ X = \text{anion} \]

from cell edge
\[ a = 2r_M + 2r_X \]

from face diagonal
\[ a = 2\sqrt{2}r_X \]

\[ r_M + r_X = r_X\sqrt{2} \]
\[ r_M/r_X = \sqrt{2} - 1 = 0.414 \]

The cavity radius is 41% of the anion radius.
SIZE OF TETRAHEDRAL CAVITY

The tetrahedral holes are twice as numerous but six times smaller in volume.

The cavity radius is 22.5% of the anion radius.

\[ r_M + r_X = r_X \cdot \frac{1}{2} \sqrt{6} \]
\[ r_M / r_X = \frac{1}{2} \sqrt{6} - 1 = 0.225 \]
EUTACTIC STRUCTURES

Structures in which the arrangement of ions is the same as in a close packed array but the ions are not necessarily touching

Within certain loose limits (given by the *radius ratio rules*), cations too large to fit in the interstices can be accommodated by an expansion of the anion array

- *anions don’t like to touch anyway*

- *modern techniques show that, in many cases, anions (cations) are not as large (small) as previously thought*

- *we still describe eutactic structures as CCP or HCP lattices with ions in some fraction of the interstitial sites*
CRYSTALS THAT CAN BE DESCRIBED IN TERMS OF INTERSTITIAL FILLING OF A CLOSE-PACKED STRUCTURE
SOME EUTACTIC CRYSTAL STRUCTURES

Variables:
1) anion layer stacking sequence: CCP or HCP array?
2) occupancy of interstitial sites

<table>
<thead>
<tr>
<th>Anion arrangement</th>
<th>Interstitial sites</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_+$</td>
<td>$T_-$</td>
</tr>
<tr>
<td>c.c.p.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\frac{1}{8}$</td>
<td>$\frac{1}{8}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>h.c.p.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\frac{1}{2}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\frac{1}{8}$</td>
<td>$\frac{1}{8}$</td>
</tr>
<tr>
<td></td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c.c.p. ‘CaO$_3$’ layers</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*The h.c.p. oxide layers in rutile and $\gamma$-Li$_3$PO$_4$ are not planar but are buckled. The oxide ion arrangement in these may alternatively be described as tetragonal packed (t.p.).
### Structures obtained by filling Octahedral Holes

<table>
<thead>
<tr>
<th>Structure</th>
<th>Fraction Holes Filled</th>
<th>Packing</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>1</td>
<td>ccp</td>
</tr>
<tr>
<td>NiAs</td>
<td>1</td>
<td>hcp</td>
</tr>
<tr>
<td>CdCl₂</td>
<td>1/2</td>
<td>ccp</td>
</tr>
<tr>
<td>CdI₂</td>
<td>1/2</td>
<td>hcp</td>
</tr>
<tr>
<td>TiO₂⁺</td>
<td>1/2</td>
<td>hcp</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>2/3</td>
<td>hcp</td>
</tr>
</tbody>
</table>

### Structures obtained by filling Tetrahedral Holes

<table>
<thead>
<tr>
<th>Structure</th>
<th>Fraction Holes Filled</th>
<th>Packing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorite†</td>
<td>1</td>
<td>ccp</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>1/2</td>
<td>ccp</td>
</tr>
<tr>
<td>Wurtzite</td>
<td>1/2</td>
<td>hcp</td>
</tr>
</tbody>
</table>

†In fluorite (i.e. CaF₂) the cations are close packed and the anions fill the tetrahedral holes. The opposite is true of the antifluorite structure (Na₂O)

† The hcp anion layers are buckled in rutile.
**NaCl (ROCK SALT, HALITE) STRUCTURE**

**Space Group** = Fm$\bar{3}$m
**Lattice** = FCC
**Basis** = Cl (0,0,0), Na ($\frac{1}{2},\frac{1}{2},\frac{1}{2}$)

**Coordination** = 6, 6
Cation Coord. → Octahedron
Anion Coord. → Octahedron
Connectivity → Edge sharing octahedra with faces parallel to {111}

4 NaCl in unit cell
POLYHEDRAL REPRESENTATION

- shows the topology and indicates interstitial sites
- tetrahedra and octahedra are the most common shapes

Rock Salt:

- Array of edge sharing NaCl₆ octahedra
- Each octahedron shares all 12 edges
- Tetrahedral interstices

Galena (PbS)
• Very common (inc. 'ionics', 'covalents' & 'intermetallics')
• Most alkali halides (CsCl, CsBr, CsI excepted)
• Most oxides / chalcogenides of alkaline earths
• Many nitrides, carbides, hydrides (e.g. ZrN, TiC, NaH)
COMPLEX ION VARIANT OF ROCK SALT

- space group = Pa\(_3\)
- \(S_2^{2-}\) dimers oriented along \(<111>\)
ZINC BLENDE (ZnS, SPHALERITE)

(CCP, T+ Holes Filled)

Space Group = F43m
Lattice = FCC
Basis = S (0,0,0), Zn (¼,¼,¼)

Coordination = 4, 4
Cation Coord. → Tetrahedron
Anion Coord. → Tetrahedron
Connectivity → Corner sharing Tetra.
4 ZnS in unit cell
ZINC BLENDE

- bonding is less ionic than in rock salt
- common for Be, Zn, Cd, Hg chalcogenides (i.e., ZnS, ZnSe, ZnTe)
- common for III-V compounds (B, Al, Ga, In with N, P, As, Sb)

<table>
<thead>
<tr>
<th>Material</th>
<th>$a(\text{Å})$</th>
<th>$a(\text{Å})$</th>
<th>$a(\text{Å})$</th>
<th>$a(\text{Å})$</th>
<th>$a(\text{Å})$</th>
<th>$a(\text{Å})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuF</td>
<td>4.255</td>
<td>BeS</td>
<td>4.8624</td>
<td>CdS</td>
<td>5.818</td>
<td>BN</td>
</tr>
<tr>
<td>CuCl</td>
<td>5.416</td>
<td>BeSe</td>
<td>5.07</td>
<td>CdSe</td>
<td>6.077</td>
<td>BP</td>
</tr>
<tr>
<td>$\gamma$-CuBr</td>
<td>5.6905</td>
<td>BeTe</td>
<td>5.54</td>
<td>CdTe</td>
<td>6.481</td>
<td>BAs</td>
</tr>
<tr>
<td>$\gamma$-CuI</td>
<td>6.051</td>
<td>$\beta$-ZnS</td>
<td>5.4060</td>
<td>HgS</td>
<td>5.8517</td>
<td>AlP</td>
</tr>
<tr>
<td>$\gamma$-AgI</td>
<td>6.495</td>
<td>ZnSe</td>
<td>5.667</td>
<td>HgSe</td>
<td>6.085</td>
<td>AlAs</td>
</tr>
<tr>
<td>$\beta$-MnS, red</td>
<td>5.600</td>
<td>ZnTe</td>
<td>6.1026</td>
<td>HgTe</td>
<td>6.453</td>
<td>AlSb</td>
</tr>
<tr>
<td>$\beta$-MnSe</td>
<td>5.88</td>
<td>$\beta$-SiC</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**DIAMOND STRUCTURE**

Same as sphalerite, but with identical atoms in all positions

- **Space Group** = F43m
- **Lattice** = FCC
- **Basis** = C (0,0,0), C (¼,¼,¼)

**Coordination** = 4
Connectivity → Corner sharing Tetra.
8 C atoms per unit cell

<table>
<thead>
<tr>
<th>Table 1.9 Elemental Crystals with the Diamond Crystal Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
</tr>
<tr>
<td>---------</td>
</tr>
<tr>
<td>C</td>
</tr>
<tr>
<td>Ge</td>
</tr>
</tbody>
</table>

$^a$Lattice constants are values at room temperature.
**FLUORITE (CaF$_2$) & ANTIFLUORITE (Na$_2$O)**

**Fluorite** : CCP of Ca$^{2+}$, 100% Tetra. HolesFilled with F$^-$

**Anti-fluorite** : cation and anion positions are reversed

- **Space Group** = Fm$\bar{3}$m
- **Lattice** = FCC
- **Basis** = Ca$^{2+}$ (0,0,0), F$^-$ ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$) & ($\frac{3}{4}, \frac{3}{4}, \frac{3}{4}$)

**Coordination** = 8, 4 (fluorite)
- Cation Coord. → Cubic
- Anion Coord. → Tetrahedral

Connectivity → Edge sharing FCa$_4$ tetrahedra or edge sharing CaF$_8$ cubes

4 CaF$_2$ in unit cell
ALTERNATIVE REPRESENTATIONS

Displacing the unit cell by $\frac{1}{4}$ of a body diagonal emphasizes the cubic cation coordination:

Fluorite A-cell

Plan view

FCa$_4$ Tetrahedra

Fluorite B-cell

Plan view

CaF$_8$ Cubes
• origin of the term “fluorescence” (George Stokes, 1852)

• fluorite common for fluorides of large, divalent cations and oxides of large tetravalent cations (M$^{2+}$F$_2$ and M$^{4+}$O$_2$)

• antifluorite common for oxides/chalcogenides of alkalis (M$_2$O)
FLUORESCENT MINERALS

= fluorite

http://en.wikipedia.org/wiki/Fluorescence
COMPARING NaCl, ZnS, Na₂O
Li$_3$Bi EXAMPLE

ccp

filling of all $O_h$ and $T_d$ voids

Li$_3$Bi type

$C_{60}$

$K_3C_{60}$
**NiAs STRUCTURE**

(HCP, 100% Oct. Holes Filled)

**Space Group** = P6$_3$/mmc

**Lattice** = Primitive hexagonal

**Basis** = As (0,0,0) & (2/3,1/3,1/2)  
Ni (1/3,2/3,1/4) & (1/3,2/3,3/4)

**Coordination** = 6, 6

Cation Coord. → Octahedron

Anion Coord. → Trigonal prism

Connectivity → Edge/face sharing Oct.  
or edge-sharing trigonal prisms

2 NiAs in unit cell
Alternative unit cell with Ni at the origin:
NiAs

- Transition metals with chalcogens, As, Sb, Bi
  e.g. Ti(S,Se,Te);
  Cr(S,Se,Te,Sb);
  Ni(S,Se,Te,As,Sb,Sn)
WURTZITE (ZnS) STRUCTURE

(HCP, T+ Holes Filled)

**Space Group** = P6₃mc

**Lattice** = Primitive hexagonal

**Basis** = S (0,0,0) & (2/3,1/3,1/2)  
Zn (0,0,5/8) & (2/3,1/3,1/8)

**Coordination** = 4, 4

Cation Coord. → Tetrahedron  
Anion Coord. → Tetrahedron  
Connectivity → Corner sharing Tetra.  
2 ZnS in unit cell

<table>
<thead>
<tr>
<th>Compound</th>
<th>a(Å)</th>
<th>u</th>
<th>c/a</th>
<th>b(Å)</th>
<th>c/a</th>
<th>u</th>
<th>c/a</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>3.2495</td>
<td>0.345</td>
<td>1.602</td>
<td>4.580</td>
<td>7.494</td>
<td>1.636</td>
<td></td>
</tr>
<tr>
<td>ZnS</td>
<td>3.811</td>
<td>0.378</td>
<td>1.623</td>
<td>3.111</td>
<td>4.978</td>
<td>0.385</td>
<td>1.600</td>
</tr>
<tr>
<td>ZnSe</td>
<td>3.98</td>
<td>0.378</td>
<td>1.623</td>
<td>3.076</td>
<td>5.048</td>
<td>0.365</td>
<td>1.600</td>
</tr>
<tr>
<td>ZnTe</td>
<td>4.27</td>
<td>0.378</td>
<td>1.623</td>
<td>3.533</td>
<td>5.693</td>
<td>1.611</td>
<td></td>
</tr>
<tr>
<td>BeO</td>
<td>2.698</td>
<td>0.378</td>
<td>1.623</td>
<td>3.111</td>
<td>4.978</td>
<td>0.385</td>
<td>1.600</td>
</tr>
<tr>
<td>CdS</td>
<td>4.1348</td>
<td>0.378</td>
<td>1.623</td>
<td>4.39</td>
<td>7.02</td>
<td>0.365</td>
<td>1.600</td>
</tr>
<tr>
<td>CdSe</td>
<td>4.30</td>
<td>0.378</td>
<td>1.623</td>
<td>3.076</td>
<td>5.048</td>
<td>1.641</td>
<td></td>
</tr>
<tr>
<td>MnS</td>
<td>3.976</td>
<td>0.378</td>
<td>1.618</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MnSe</td>
<td>4.12</td>
<td>0.378</td>
<td>1.631</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Projections perpendicular to close-packed planes

**Zinc Blende**

*CCP* *ABC repeat*

**Wurtzite**

*HCP* *AB repeat*
POLYHEDRAL REPRESENTATIONS

Zinc Blende
Vertex-linked tetrahedra only, but layers skewed in Wurtzite, & not in Blende

Wurtzite
Very different next-nearest neighbor coordinations & beyond
HCP VERSION OF CaF$_2$?

No structures are known with all Tetra. sites (T+ and T-) filled in HCP - i.e. there is no HCP analogue of the Fluorite / Anti-Fluorite structure

Why?

The T+ and T- interstitial sites above and below a layer of close-packed spheres in HCP are too close to each other (distance = 0.25c) to tolerate the coulombic repulsion generated by filling with like-charged ions.

Face-linking is unfavorable
RUTILE STRUCTURE (TiO\textsubscript{2})

(distorted HCP, 50% Oct. Holes Filled)

Space Group = P4\textsubscript{2}/nmn

Lattice = Primitive tetragonal

Basis = Ti (0,0,0) & (½,½,½)
O (0.3,0.3,0), (0.7,0.7,0), (0.8,0.2,0.5), (0.2,0.8,0.5)

Coordination = 6, 3
Cation Coord. → Octahedral
Anion Coord. → Trigonal planar
Connectivity → chains of edge-sharing Oct. along c axis, linked by vertices
2 TiO\textsubscript{2} per unit cell
ANATASE STRUCTURE (TiO$_2$)

**Space Group** = I4$_1$/amd

**Lattice** = body-centered tetragonal

**Coordination** = 6, 3
- Cation Coord. → Octahedral
- Anion Coord. → Trigonal planar
- Connectivity → chains of edge-sharing Oct.
  - along c axis, linked by vertices and edges
4 TiO$_2$ per unit cell

Volume anatase TiO$_2$ cell: 136.25 Å$^3$

rutile TiO$_2$ cell: 62.07 Å$^3$

a = 3.776 Å
b = 3.776 Å
c = 9.486 Å
RUTILE AND ANATASE

chains of edge sharing oct., linked at corners

greater density of edge sharing → a bit less stable
CdI$_2$ STRUCTURE

(HCP, with Cd in Oct. Holes of alternate layers)

Space Group = $\overline{P}\overline{3}m1$
Lattice = Primitive trigonal
Basis = Cd (0,0,0)
       I (2/3,1/3,1/4) & (1/3,2/3,3/4)
Coordination = 6, 3
Cation Coord. → Octahedron
Anion Coord. → Trigonal pyramid
Connectivity → sheets of edge-sharing Oct.
1 CdI$_2$ per unit cell

Table 7.13 Some compounds with the CdI$_2$ structure. (Data taken from Wyckoff, 1971, Vol. 1)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$a$(Å)</th>
<th>$c$(Å)</th>
<th>$a$(Å)</th>
<th>$c$(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdI$_2$</td>
<td>4.24</td>
<td>6.84</td>
<td>3.768</td>
<td>6.180</td>
</tr>
<tr>
<td>CaI$_2$</td>
<td>4.48</td>
<td>6.96</td>
<td>3.629</td>
<td>6.492</td>
</tr>
<tr>
<td>CoI$_2$</td>
<td>3.96</td>
<td>6.65</td>
<td>3.82</td>
<td>6.19</td>
</tr>
<tr>
<td>FeI$_2$</td>
<td>4.04</td>
<td>6.75</td>
<td>3.74</td>
<td>6.17</td>
</tr>
<tr>
<td>MgI$_2$</td>
<td>4.14</td>
<td>6.88</td>
<td>3.68</td>
<td>6.12</td>
</tr>
<tr>
<td>MnI$_2$</td>
<td>4.16</td>
<td>6.82</td>
<td>3.561</td>
<td>5.875</td>
</tr>
<tr>
<td>PbI$_2$</td>
<td>4.555</td>
<td>6.977</td>
<td>3.601</td>
<td>5.835</td>
</tr>
<tr>
<td>ThI$_2$</td>
<td>4.13</td>
<td>7.02</td>
<td>3.147</td>
<td>4.769</td>
</tr>
<tr>
<td>TiI$_2$</td>
<td>4.110</td>
<td>6.820</td>
<td>3.584</td>
<td>4.896</td>
</tr>
<tr>
<td>TmI$_2$</td>
<td>4.520</td>
<td>6.967</td>
<td>3.258</td>
<td>4.605</td>
</tr>
<tr>
<td>VI$_2$</td>
<td>4.000</td>
<td>6.70</td>
<td>3.173</td>
<td>4.640</td>
</tr>
<tr>
<td>YbI$_2$</td>
<td>4.503</td>
<td>6.972</td>
<td>3.117</td>
<td>4.595</td>
</tr>
<tr>
<td>ZnI$_2$(I)</td>
<td>4.25</td>
<td>6.54</td>
<td>3.48</td>
<td>4.67</td>
</tr>
</tbody>
</table>

A layered crystal
Alternative unit cell with Cd at the origin:

Comparison

$\text{CdI}_2$ vs $\text{NiAs}$

$\text{CdI}_6$ units

$\text{NiAs}_6$ units
CdI₂ - OCCURANCE

- Iodides of moderately polarizing cations; bromides and chlorides of strongly polarizing cations;  
  *e.g.* PbI₂, FeBr₂, VCl₂

- Hydroxides of many divalent cations  
  *e.g.* (Mg,Ni)(OH)₂

- Di-chalcogenides of many quadrivalent cations  
  *e.g.* TiS₂, ZrSe₂, CoTe₂
CdCl₂ STRUCTURE

The CCP analogue of CdI₂

(CCp, with Cd in Oct. Holes of alternate layers along [111])

Space Group = $\overline{R}32/m$

Chlorides of moderately polarizing cations
e.g. MgCl₂, MnCl₂

Di-sulfides of quadrivalent cations
e.g. TaS₂, NbS₂ (CdI₂ form as well)

Table 7.14 Some compounds with the CdCl₂ structure. (Data taken from Wyckoff, 1971, Vol. 1)

<table>
<thead>
<tr>
<th>Compound</th>
<th>a(Å)</th>
<th>c(Å)</th>
<th>a(Å)</th>
<th>c(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdCl₂</td>
<td>3.854</td>
<td>17.457</td>
<td>NiCl₂</td>
<td>3.543</td>
</tr>
<tr>
<td>CdBr₂</td>
<td>3.95</td>
<td>18.67</td>
<td>NiBr₂</td>
<td>3.708</td>
</tr>
<tr>
<td>CoCl₂</td>
<td>3.544</td>
<td>17.430</td>
<td>NiI₂</td>
<td>3.892</td>
</tr>
<tr>
<td>FeCl₂</td>
<td>3.579</td>
<td>17.536</td>
<td>ZnBr₂</td>
<td>3.92</td>
</tr>
<tr>
<td>ZnCl₂</td>
<td>3.596</td>
<td>17.589</td>
<td>ZnI₂</td>
<td>4.25</td>
</tr>
<tr>
<td>MnCl₂</td>
<td>3.686</td>
<td>17.470</td>
<td>Cs₂O*</td>
<td>4.256</td>
</tr>
</tbody>
</table>

*Cs₂O has an anti-CdCl₂ structure.
<table>
<thead>
<tr>
<th>Formula</th>
<th>Type and fraction of sites occupied</th>
<th>CCP</th>
<th>HCP</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB</td>
<td>All octahedral</td>
<td>NaCl <em>Rock Salt</em></td>
<td>NiAs <em>Nickel Arsenide</em></td>
</tr>
<tr>
<td></td>
<td>Half tetrahedral (T+ or T-)</td>
<td>ZnS <em>Zinc Blende</em></td>
<td>ZnS <em>Wurtzite</em></td>
</tr>
<tr>
<td>A₂B</td>
<td>All tetrahedral</td>
<td>Na₂O <em>Anti-Fluorite</em></td>
<td>not known</td>
</tr>
<tr>
<td>A₃B</td>
<td>All octahedral &amp; tetrahedral</td>
<td>Li₃Bi</td>
<td>not known</td>
</tr>
<tr>
<td>AB₂</td>
<td>Half octahedral (Alternate layers full/empty)</td>
<td>CdCl₂ <em>(Cadmium Chloride)</em></td>
<td>CdI₂ <em>(Cadmium Iodide)</em></td>
</tr>
<tr>
<td></td>
<td>Half octahedral (Ordered framework arrangement)</td>
<td>TiO₂ <em>(Anatase)</em></td>
<td>CaCl₂</td>
</tr>
<tr>
<td></td>
<td>Third octahedral Alternate layers 2/3 full/empty</td>
<td>YCl₃</td>
<td>TiO₂ <em>(Rutile)</em></td>
</tr>
<tr>
<td></td>
<td></td>
<td>BiI₃</td>
<td></td>
</tr>
</tbody>
</table>
PEROVSKITE STRUCTURE ABX$_3$ (CaTiO$_3$)

(CCP of Ca & O, 25% Oct. Holes Filled by Ti)

**Space Group** = Pm3m

**Lattice** = Primitive cubic

**Basis** = Ti (0,0,0), Ca ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$), O ($\frac{1}{2}, 0, 0$), (0,1/2,0) & (0,0,1/2)

**Coordination** = Ca-12; Ti-6; O-6

Ca Coord. → Cuboctahedron

Ti Coord. → Octahedron

O Coord. → distorted octahedron (4 Ca, 2 Ti)

1 CaTiO$_3$ per unit cell

An extremely rich, important class of compounds:

- Magnetoresistance
- Ferroelectricity
- Multiferroics
- Superconductivity
- Catalysis (fuel cells)
- Spin transport

129
PEROVSKITE CONNECTIVITY

3D network of corner-sharing octahedra

Network of face-sharing cuboctahedra

B-Cell

TiO$_6$ octahedra

CaO$_{12}$ cuboctahedra
Perovskites: the most widely studied oxide structure

- Wide range of chemistries possible
  - thousands of examples known
- Cubic, tetragonal, and orthorhombic symmetries are common

Unique properties of perovskites

- high $T_c$ cuprate superconductors
- Colossal Magneto-Resistance ($\text{La, SrMnO}_3$)
- fast ion conduction ($\text{Li}^+$, $\text{O}^{2-}$ in $\text{SrSnO}_3$), batteries, fuel cells
- mixed electronic/ionic conduction, fuel cells
- oxidation/reduction catalysts
- ferroelectric / piezoelectric ceramics ($\text{BaTiO}_3$, $\text{Pb(ZrTiO}_3$)
- important mineral structure in lower mantle ($\text{MgSiO}_3$, pyroxene)
- frequency filters for wireless communications: $\text{Ba(Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$
Perovskite Structure: \(ABX_3\)

Tolerance factor (\(t\)):

\[
t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)}
\]

<table>
<thead>
<tr>
<th>(t)</th>
<th>Effect</th>
<th>Likely structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt; 1</td>
<td>A cation too large to fit in interstices</td>
<td>Hexagonal perovskite</td>
</tr>
<tr>
<td>0.9 - 1.0</td>
<td>ideal</td>
<td>Cubic perovskite</td>
</tr>
<tr>
<td>0.71 - 0.9</td>
<td>A cation too small</td>
<td>Orthorhombic perovskite</td>
</tr>
<tr>
<td>&lt; 0.71</td>
<td>A cation same size as B cation</td>
<td>Possible close packed lattice</td>
</tr>
</tbody>
</table>
Most perovskites contain distorted octahedra and are not cubic, at least at lower temperatures. These distortions give perovskites a rich physics.

### BaTiO$_3$:  
- $\text{Ba}^{2+}$: $r = 1.56$ Å  
- $\text{Ti}^{4+}$: $r = 0.68$ Å  
- $\text{O}^{2-}$: $r = 1.26$ Å  

### KNbO$_3$:  
- $\text{K}^+$: $1.65$ Å  
- $\text{Nb}^{5+}$: $0.78$ Å  

### LiNbO$_3$:  
- $\text{Li}^+$: $1.06$ Å  
- $\text{Nb}^{5+}$: $0.78$ Å  

**Symmetry at $25^\circ$C**

- $t = 1.03$ - tetragonal
- $t = 1.01$ - orthorhombic
- $t = 0.81$ - trigonal

LiNbO$_3$ : *ferroelectricity*, Pockels effect, piezoelectricity, photoelasticity, nonlinear optical polarizability
Figure 3.7: Perovskite distortion from (a) cubic to (b) orthorhombic.
What is a Ferroelectric

A ferroelectric material develops a spontaneous polarization (builds up a charge) in response to an external electric field.

- The polarization does not go away when the external field is removed.
- The direction of the polarization is reversible.

Applications of Ferroelectric Materials
- Multilayer capacitors
- Non-volatile FRAM (Ferroelectric Random Access Memory)
DI-, PARA-, AND FERROELECTRICS

dielectric polarization: $P = \varepsilon_0 \chi_e E$

- linear: $P = \varepsilon_0 \chi_e E$
- no $P$ without $E$

paraelectric polarization: $P = \Sigma p/V$

- nonlinear
- no $P$ without $E$

ferroelectric polarization

- residual (zero-field) polarization
- reversible direction of residual $P$
- very large susceptibilities

$d$ dipole moment: $p = qd = \alpha E$

- polarization ($C/m^2$)
- $\varepsilon_0$: vacuum permittivity - $8.85 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$
- $\chi_e$: electric susceptibility (unitless)
- $E$: electric field ($V/m$, or $N/C$)
WHY IS BaTiO₃ FERROELECTRIC

• Ba²⁺ is larger than the vacancy in the octahedral network tolerance factor > 1.
• This expands the octahedron, which leads to a shift of Ti⁴⁺ toward one of the corners of the octahedron.
• The direction of the shift can be altered through application of an electric field.

> 120°C cubic, not FE
< 120°C tetragonal, FE

transition occurs at the Curie temperature, \( T_c \)

~0.1 Å displacement
**BaTiO$_3$ Phase Transitions**

In the cubic structure BaTiO$_3$ is paraelectric. That is to say that the orientations of the ionic displacements are not ordered and dynamic.

Below 393 K BaTiO$_3$ becomes ferroelectric and the displacement of the Ti$^{4+}$ ions progressively displace upon cooling.

\[
\epsilon_r = \chi_e + 1
\]

FERROELECTRIC HYSTERESIS LOOPS

remnant polarization, $P_R$

saturation polarization, $P_s$

coercive field, $E_C$

dipoles aligned “up”

dipoles aligned “down”

Fig. 15.12 Hysteresis loop of a ferroelectric. The dashed line passing through the origin represents the behaviour of normal dielectric materials.
ORDERED ELECTRIC DIPOLE PHASES

ferroelectric (BaTiO$_3$)
- parallel ordering below $T_c$

antiferroelectric (PbZrO$_3$)
- antiparallel ordering below $T_c$

E field can induce ferroelectric state

ferrielectric (Bi$_4$Ti$_3$O$_{12}$)
- net spontaneous polarization in only certain direction(s)
CURIE TEMPERATURE

Thermal energy destroys the ordered electric dipole state. The temperature above which this *order-disorder phase transition* occurs is the *Curie temperature, $T_c$.*

Above $T_c$, the material is often paraelectric.

![Diagram showing Curie temperature and phase transitions](image)

*Fig. 15.15 Dielectric constant of BaTiO$_3$ ceramic*

**Note:** These curves omit the "spikes" in $P$ at $T_c$.
PHASE DIAGRAMS

Table 15.2 Some ferroelectric materials

<table>
<thead>
<tr>
<th>Material</th>
<th>( T_d (^\circ \text{C}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium titanate, ( \text{BaTiO}_3 )</td>
<td>120</td>
</tr>
<tr>
<td>Rochelle salt, ( \text{KNa}<em>2\text{C}</em>{12}\text{H}_2\text{O}_6\cdot 4\text{H}_2\text{O} )</td>
<td>Between (-18) and (+24)</td>
</tr>
<tr>
<td>Potassium niobate, ( \text{KNbO}_3 )</td>
<td>434</td>
</tr>
<tr>
<td>Potassium dihydrogen phosphate, ( \text{KDP}, \text{KH}_2\text{PO}_4 )</td>
<td>(-150)</td>
</tr>
<tr>
<td>Lead titanate, ( \text{PbTiO}_3 )</td>
<td>490</td>
</tr>
<tr>
<td>Lithium niobate, ( \text{LiNbO}_3 )</td>
<td>1210</td>
</tr>
<tr>
<td>Bismuth titanate, ( \text{Bi}_4\text{Ti}<em>3\text{O}</em>{12} )</td>
<td>675</td>
</tr>
<tr>
<td>Gadolinium molybdate, ( \text{GMO}, \text{Gd}_2(\text{MoO}_4)_3 )</td>
<td>159</td>
</tr>
<tr>
<td>Lead zirconate titanate, PZT, ( \text{Pb}(\text{Zr},\text{Ti}_{1-x})\text{O}_3 )</td>
<td>Depends on ( x )</td>
</tr>
</tbody>
</table>
K$_2$NiF$_4$ STRUCTURE (La$_2$CuO$_4$)

Many “complex” structures are composed of simple, familiar building blocks. The high-$T_c$ copper oxide superconductors are an example.

Doped La$_2$CuO$_4$ was the first (1986) High-$T_c$ Superconducting Oxide ($T_c \sim 40$ K) Bednorz & Müller were awarded a Nobel Prize

La$_2$CuO$_4$ may be viewed as if constructed from an ABAB... arrangement of Perovskite cells - known as an AB Perovskite!
We may view the structure as based on:
1. Sheets of elongated CuO$_6$ octahedra, sharing only vertices
2. Layered networks of CuO$_4$$^{6-}$, connected by La$^{3+}$ ions
Common structural form of vertex-linked CuO$_4$ squares

- This motif occurs in all the high-$T_c$ superconducting copper oxides
- The structures differ in the structure of the 'filling' in the 'sandwich' of copper oxide layers - known as **Intergrowth Structures**
Y$_1$Ba$_2$Cu$_3$O$_7$: THE 1,2,3 SUPERCONDUCTOR

- the first material to superconduct at LN$_2$ temperature, $T_c > 77$ K
- YBa$_2$Cu$_3$O$_7$ can be viewed as an Oxygen-Deficient Perovskite
Two types of Cu sites:
1) Layers of $\text{CuO}_5$ square pyramids
2) Chains of vertex-linked $\text{CuO}_4$ squares
SPINEL STRUCTURE AB$_2$O$_4$ (MgAl$_2$O$_4$)

(CCP, Mg in 1/8$^{th}$ of Tetra. Holes and Al in 50% of Oct. Holes)

Space Group = Fd$ar{3}$m
Lattice = FCC
Coordination = Mg-4; Al-6; O-4
Mg Coord. → Tetrahedron
Al Coord. → Octahedron
Connectivity → chains of edge-sharing AlO$_6$ octahedra, linked by MgO$_4$ tetra.
8 MgAl$_2$O$_4$ per unit cell (56 atoms)

• extremely flexible structure, adopted by 100s of compounds

• normal spinel: 8 A in Tetra., 16 B in Oct.

• inverse spinel: 8 B in Tetra, 8 A and 8 B in Oct.

intermediate cations distributions also occur.
The unit cell of the spinel structure formula

\[ \text{AB}_2\text{O}_4 \text{ spinel} \] The red cubes are also contained in the back half of the unit cell.
SPINELS - OCCURANCE

Aluminium spinels:
- Spinel - $\text{MgAl}_2\text{O}_4$, after which this class of minerals is named
- Gahnite - $\text{ZnAl}_2\text{O}_4$
- Hercynite - $\text{FeAl}_2\text{O}_4$

Iron spinels:
- Magnetite - $\text{Fe}_3\text{O}_4$
- Franklineite - $(\text{Fe, Mn, Zn})(\text{Fe, Mn})_2\text{O}_4$
- Ullöspinel - $\text{TiFe}_2\text{O}_4$
- Jacobsite - $\text{MnFe}_2\text{O}_4$
- Trevorite - $\text{NiFe}_2\text{O}_4$

Chromium spinels:
- Chromite - $\text{FeCr}_2\text{O}_4$
- Magnesiochromite - $\text{MgCr}_2\text{O}_4$

Others with the spinel structure:
- Ullöspinel - $\text{Fe}_2\text{TiO}_4$
- Ringwoodite - $\text{Mg}_2\text{SiO}_4$, an abundant olivine polymorph within the Earth's mantle from about 520 to 660 km depth, and a rare mineral in meteorites

Table 5.2. Composition and cell size of the more common thiospinels

<table>
<thead>
<tr>
<th>Composition</th>
<th>Cell size $a$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linnaeite</td>
<td>Co$_2$S$_4$</td>
</tr>
<tr>
<td>Polydymite</td>
<td>Ni$_3$S$_4$</td>
</tr>
<tr>
<td>Siegenite</td>
<td>(Co,Ni)$_3$S$_4$</td>
</tr>
<tr>
<td>Greigite</td>
<td>Fe$_3$S$_4$</td>
</tr>
<tr>
<td>Violarite</td>
<td>FeNi$_2$S$_4$</td>
</tr>
<tr>
<td>Carrollite</td>
<td>CuCo$_2$S$_4$</td>
</tr>
<tr>
<td>Daubréelite</td>
<td>FeCr$_2$S$_4$</td>
</tr>
<tr>
<td>Indite</td>
<td>InFe$_2$S$_4$</td>
</tr>
</tbody>
</table>
CRYSTAL FIELD STABILIZATION ENERGY

In transition metal compounds, $d$ electron effects such as crystal field stabilization energy (CFSE) can be important in determining structure.

**Crystal field splitting diagrams**

- **Octahedral Field**
  - Degenerate $d$ orbitals: $t_{2g}$, $e_g$
  - Energy splitting: $\Delta_{oct} = 4Dq$
  - CFSE formula: $CFSE_{oct} = (0.4 \times \#t_{2g} - 0.6 \times \#e_g) \Delta_{oct}$

- **Tetrahedral Field**
  - Degenerate $d$ orbitals: $t_2$, $e$
  - Energy splitting: $\Delta_{tetra} = 4Dq$
  - Formula: $\Delta_{tetra} = (4/9)\Delta_{oct}$

**Diagram**

- *Fig. 8.9* Splitting of $d$ energy levels in (a) an octahedral and (b) a tetrahedral field.

- *Graph* showing lattice energy vs. number of $d$ electrons for transition metals, with no CFSE for a specific compound.
CATION SITE PREFERENCES IN SPINELS

In the absence of CFSE effects: 2,3 spinels tend to be normal (MgAl2O4) 4,2 spinels tend to be inverse (TiMg2O4)

In 2,3 spinels, CFSE favors the following:

1) Chromium spinels (Cr3+) are normal
2) Magnetite (Fe3O4) is inverse b/c Fe3+ has zero CFSE, while Fe2+ prefers oct.
3) Mn3O4 is normal b/c Mn2+ has no CFSE

The larger CFSE of metal ions in octahedral sites is sometimes an important factor in determining spinel structures (normal vs inverse).

In the absence of CFSE effects: 2,3 spinels tend to be normal (MgAl2O4) 4,2 spinels tend to be inverse (TiMg2O4)

In 2,3 spinels, CFSE favors the following:

1) Chromium spinels (Cr3+) are normal
2) Magnetite (Fe3O4) is inverse b/c Fe3+ has zero CFSE, while Fe2+ prefers oct.
3) Mn3O4 is normal b/c Mn2+ has no CFSE
CORUNDUM STRUCTURE ($\alpha$-Al$_2$O$_3$)

(HCP, 2/3 of Oct. Holes filled)

**Space Group** = $\overline{R}3c$

**Lattice** = Primitive trigonal

**Coordination** = 6, 4
Cation Coord. $\rightarrow$ Octahedron
Anion Coord. $\rightarrow$ distorted tetrahedron
Connectivity $\rightarrow$ edge, face-sharing Oct.
6 Al$_2$O$_3$ per unit cell

- Ruby (Cr), sapphire (Fe, Ti, Cr), Fe$_2$O$_3$