Solid State Theory
Physics 545
CRYSTAL STRUCTURES

Describing periodic structures

• Terminology
• Basic Structures
• Symmetry Operations
Ionic crystals often have a definite habit which gives rise to particular crystal shapes with particular crystallographic faces dominating and easy cleavage planes present.

Single crystal of NaCl being cleaved with a razor blade
Early observations of the regular shapes of crystals and their preferred cleavage plans lead to the suggestion that they are built up from simple units.

This suggestion was made long before the atomic theory of matter was developed. For example the pictures below are from a work on the form of crystals from R.J.Hauy in 1801.
The unit cell shape must fill space and so there are restrictions on the cell shapes that can be used.

For example in 2-Dimensions it is not possible to have a pentagonal unit cell.
The repeating pattern of atoms in a crystal can be used to define a **unit cell**.

This is a small volume of the material that can be translated through space to reproduce the entire crystal.

The translation of the unit cell follows the vectors given by its sides, these are the cell vectors (2D $a$ & $b$, in 3D $a, b$ & $c$).

If the unit cell contains only one formula unit it is a **primitive cell**.
Crystallography is largely based on Group Theory (symmetry).
Symmetry operations transform space into itself. Simplest symmetry operator is the unity operator (= does nothing).
(=Lattice is invariant with respect to symmetry operations)
Translation operator, $T_R$, replaces radius vector of every point, $r$, by $r' = r + R$. 
The unit cell is the basic repeat unit for the crystal.

If each unit cell is thought of as a single point the crystal can be simplified to a **lattice**.

We can always move to an equivalent point in a lattice by taking an integer combination of the lattice vectors:

\[ \overrightarrow{T} = u\overrightarrow{a} + v\overrightarrow{b} + w\overrightarrow{c} \quad (u,v,w) \text{ being integers.} \]
TERMINOLOGY

- Lattice Point- Point that contains an atom or molecule
- Unit Cell- Region defined by \( a, b, c \) which when translated by integral multiple of these vectors reproduces a similar region of the crystal
- Basis Vector- A set of linearly independent vectors \((a, b, c)\) which can be used to define a unit cell
A two-dimensional lattice showing translation of a unit cell by \( r = 3a + 2b \).
Unit Cells

Basis Vectors = 2a, 2b
Unit Cell = ODE"F"
Primitive Unit Cell = ODEF
Primitive Basis Vectors = a, b
Lattice Vector

\[ R = h\mathbf{a} + k\mathbf{b} + l\mathbf{c} \]

h, k, l are integers

Miller Indices

A displacement of any lattice point by \( R \) will give a new position in the lattice that has the same positional appearance as the original position.
A primitive cell (PC) is the smallest unit which, when repeated indefinitely in three dimensions, will generate the lattice.

A unit cell (UC) is the smallest unit that has all the symmetry elements of the lattice.

Example: BCC
Primitive cell 1 atom.
Unit cell 2 atoms = 1 + 8/8.
Symmetry: $3C_4, 4C_3, 12C_2, 6m$

$C_n$ is n-fold symmetry axis.
m is mirror plane

$i = C_2 \times m$ inversion (center of symmetry).
TERMINOLOGY

• Primitive Unit Cell- The smallest unit cell, in volume, that can be defined for a given lattice
• Primitive Basis Vectors- A set of linearly independently vectors in that can be used to define a primitive unit cell
Single species

A - G : Primitive unit cells
All have same area
All smallest unit cell
All have 1 atom/cell

a : Not a unit cell
b : Unit cell not Primitive
Multi Species

Non Primitive
2 Red, 2 green

Primitive
1 Red, 1 Green
The positions of the atoms within one unit cell are referred to as the basis of the crystal structure. To describe the whole crystal we require a lattice and a basis.

Within the unit cell the separation of two atoms will be given by:

\[ r_{12} = r_2 - r_1 \]

The crystal lattice tells us that for every pair of atoms in the atomic basis with this separation there will be an identical pair at a separation of:

\[ r'_{12} = r_2 - r_1 + T \]

Where \( T \) is any lattice vector:

\[ T = ua + vb + wc \]
A spatial arrangement of atoms (S) represents a periodic lattice if this arrangement is invariant with respect to $T_R$, where $R$ is an integer linear combination of one, two or three basic (fundamental, primitive) vectors.

$$R = n_1 a\hat{u}_1 + n_2 b\hat{u}_2 + n_2 c\hat{u}_3$$

- $n_{1,2,3}$ are any integer numbers;
- $a$, $b$ and $c$ are the lattice constants;
- $a\hat{u}_1$, $b\hat{u}_2$, $c\hat{u}_3$ are the translation vectors.

In general $u_1$, $u_2$ and $u_3$ are not orthogonal. $\alpha = u_1 u_2$, $\beta = u_2 u_3$, $\gamma = u_1 u_3$.

There are 6 parameters that define a lattice $a$, $b$, $c$, $\alpha$, $\beta$ and $\gamma$. 

$T_R(S) = S$
3 D, Bravis Lattices

- Each unit cell is such that the entire lattice can be formed by displacing the unit cell by R with no gaps in the structure (close packed)
  - i.e. structures with 3, 4 and 6 fold symmetry can be close packed. 5-fold (i.e. pentagons) cannot
- In 3 dimensions there are only 14 ways of arranging points symmetrically in space that can give no gaps
- These arrangements are the
  - BRAVIS LATTICES
- These can be further subdivided into 7 crystal structures
Figure 1.4. Notation for dimensions and angles within the unit cell of a crystal.

### THE SEVEN CRYSTAL SYSTEMS

<table>
<thead>
<tr>
<th>System</th>
<th>Unique Symmetry Element</th>
<th>Bravais Lattice</th>
<th>Unit Cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclinic</td>
<td>None</td>
<td>Simple</td>
<td>(a \neq b \neq c) (a \neq b \neq \gamma \neq 90^\circ)</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>One 2-fold rotation axis*</td>
<td>Simple</td>
<td>(a \neq b \neq c) (\alpha = \beta = 90^\circ \neq \gamma)</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>Three mutually orthogonal 2-fold rotation axes</td>
<td>Simple</td>
<td>(a \neq b \neq c) (\alpha = \beta = \gamma = 90^\circ)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Base-centered</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(\alpha = \beta = \gamma = 90^\circ)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Body-centered</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Face-centered</td>
<td></td>
</tr>
<tr>
<td>Tetragonal</td>
<td>One 4-fold rotation axis</td>
<td>Simple</td>
<td>(a = b \neq c) (\alpha = \beta = \gamma = 90^\circ)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Body-centered</td>
<td></td>
</tr>
<tr>
<td>Cubic</td>
<td>Four 3-fold rotation axes (cube diagonals)</td>
<td>Simple</td>
<td>(a = b = c) (\alpha = \beta = \gamma = 90^\circ)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Body-centered</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Face-centered</td>
<td></td>
</tr>
<tr>
<td>Hexagonal</td>
<td>One 6-fold rotation axis</td>
<td>Simple</td>
<td>(a = b \neq c) (\alpha = \beta = 90^\circ) (\gamma = 120^\circ)</td>
</tr>
<tr>
<td>Trigonal</td>
<td>One 3-fold rotation axis</td>
<td>Simple</td>
<td>(a = b = c) (\alpha = \beta = \gamma \neq 90^\circ)</td>
</tr>
</tbody>
</table>

*The term \(n\)-fold rotation axis refers to invariance under a rotation of \(360/n\) degrees about some specific axis.*
<table>
<thead>
<tr>
<th>Name</th>
<th>Number of Bravais lattices</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclinic</td>
<td>1</td>
<td>$a_1 \neq a_2 \neq a_3, \alpha \neq \beta \neq \gamma$</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>2</td>
<td>$a_1 \neq a_2 \neq a_3, \alpha = \beta = 90^\circ \neq \gamma$</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>4</td>
<td>$a_1 = a_2 = a_3, \alpha = \beta = \gamma = 90^\circ$</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>2</td>
<td>$a_1 = a_2 \neq a_3, \alpha = \beta = 90^\circ$</td>
</tr>
<tr>
<td>Cubic</td>
<td>3</td>
<td>$a_1 = a_2 = a_3, \alpha = \beta = \gamma = 90^\circ$</td>
</tr>
<tr>
<td>Trigonal</td>
<td>1</td>
<td>$a_1 = a_2 = a_3, \alpha = \beta = \gamma &lt; 120^\circ \neq 90^\circ$</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>1</td>
<td>$a_1 = a_2 \neq a_3, \alpha = \beta = 90^\circ, \gamma = 120^\circ$</td>
</tr>
</tbody>
</table>
Bravais lattices: In three dimensions there are only 14 space filling lattices, the Bravais lattices.

These are classified by 7 crystal systems (shapes):

**triclinic:**
\[ a \neq b \neq c \quad \alpha \neq \beta \neq \gamma \]

**monoclinic:**
\[ a \neq b \neq c \quad \alpha = \gamma = 90^\circ, \beta \]

**orthorhombic:**
\[ a \neq b \neq c \quad \alpha = \beta = \gamma = 90^\circ \]

**tetragonal:**
\[ a = b \neq c \quad \alpha = \beta = \gamma = 90^\circ \]

**hexagonal:**
\[ a = b \neq c \quad \alpha = \beta = 90^\circ, \gamma = 120^\circ \]

**rhombohedral:**
\[ a = b = c \quad \alpha = \beta = \gamma \]

**cubic:**
\[ a = b = c \quad \alpha = \beta = \gamma = 90^\circ \]
Bravais lattices

In addition to the shape of the unit cell a label is added to indicate the degree of centring of lattice points:

**P,C** : the cell is not centred, Primitive, only 1 lattice point.

**C** : side centred cells.

**F** : face centred cells.

**I** : body centred cells.
Cubic Lattices

BCC and FCC are not primitive. bcc has 4 atoms/cell, fcc has 8 atoms/cell
fcc has closest packing, then bcc then sc (for cubic) (fcc and bcc more common than sc)
Primitive have 1 atom/cell, Both are Rhombohedral (Trigonal)  (McKelvey p10)
Figure 1.5 Primitive unit cells for (a) the body-centered and (b) the face-centered cubic structures. In (a) the atoms are all the same despite the fact that those at the centers of the cells are highlighted to clarify spatial relationships.
Rhombohedral or Trigonal

Rhombohedral (R) Or Trigonal
\[ a = b = c, \alpha = \beta = \gamma \neq 90^\circ \]
Triclinic Monoclinic

Triclinic (Primitive)
\( a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ \)

Monoclinic (P)
\( a \neq b \neq c, \alpha = \gamma = 90^\circ, \beta \neq 90^\circ \)

Monoclinic (BaseC)
\( a \neq b \neq c, \alpha = \gamma = 90^\circ, \beta \neq 90^\circ \)
Orthorhombic

Orthorhombic (P)
\[ a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ \]

Orthorhombic (BaseC)
\[ a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ \]
Orthorhombic

Orthorhombic (BC)
\[ a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ \]

Orthorhombic (FC)
\[ a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ \]
Hexagonal

Hexagonal (P)

\[ a = b \neq c, \quad \alpha = \beta = 90^\circ, \quad \gamma = 120^\circ \]
Tetragonal

Tetragonal (P)
\[ a = b \neq c, \ \alpha = \beta = \gamma = 90^o \]

Tetragonal (BC)
\[ a = b \neq c, \ \alpha = \beta = \gamma = 90^o \]
Diamond Structure
(C, Si Ge)

- Tetrahedral bonding of carbon, Si and Ge
- Each atom bonds covalently to 4 others equally spread about atom in 3d.
- Unit cell of resulting lattice is a double fcc
- A is corner of on fcc, B is corner of second
Sodium chloride, NaCl

A *face centered cubic* arrangement of anions with the cations in all of the *octahedral* holes

8 unit cells
Space group Fm3m (225)
Fluorite, CaF$_2$

The cations lie in a *face centered cubic* arrangement and the anions occupy all of the *tetrahedral* holes.

8 unit cells
Space group Fm3m (225)
Rutile, TiO$_2$

Each titanium atom is surrounded by an approximate octahedron of oxygen atoms, and each oxygen atom is surrounded by an approximate equilateral triangle of titanium atoms.

8 unit cells
Space group P4$_2$/mnm (136)
Quartz, SiO$_2$

Each silicon atom is surrounded by a tetrahedron of oxygen atoms

4 unit cells
Space group P3$_1$21 (152)
Planes

- In all the structures, there are “planes” of atoms
  - extended surfaces on which lie regularly spaced atoms
  - These planes have many other planes parallel to them
  - These sets of planes occur in many orientations
Planes (continued)

• Orientation of Planes are identified by
  – Miller Indices (hkl)

  – Method for defining (hkl)
    • 1) Take the origin at any lattice point in the crystal, and coordinate axes in the direction of the basis vectors of the unit cell
    • 2) Locate the intercepts of a plane belonging to the desired system along each of the coordinate axes, and express them as integral multiples of a,b,c along each axis
    • 3) take the reciprocals of these numbers and multiply through by the smallest factor that will convert them to a triad of (h,k,l) having the same ratios.
• Intercepts (A,B,C) are at 2a, 4b and 3c
• reciprocal values are 1/2, 1/4 and 1/3
• Smallest common factor is 12
• \((hkl) = 12 \ (1/2,1/4,1/3) = (6,3,4)\)
• The inter-plane separation \((d_{hkl})\) is calculated from

\[
d_{hkl} = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}}\]
Miller Planes

To identify a crystal plane a set of 3 indices are used.

The Miller indices are defined by taking the intercepts of the plane with the cell vectors:

Here the intercepts are (2,3,2).

We take the inverse of the intercepts: \( \frac{1}{2}, \frac{1}{3}, \frac{1}{2} \)

The Miller indices are the lowest set integers which have the same ratio as these inverses: (323).
In cases where the plane is parallel to one or more axis the plane is taken to intercept at infinity.

Here, intercepts are $(2, \infty, \infty)$. Inverses are $\frac{1}{2}, 0, 0$

Lowest integers (100)

This shows that the plane intercepting $a$ at 2 vector lengths and parallel to $b \& c$ is equivalent to the plane intercepting at $a$. 
Figure 17  This plane intercepts the \( a, b, c \) axes at 3\( a \), 2\( b \), 2\( c \). The reciprocals of these numbers are \( \frac{1}{3}, \frac{1}{2}, \frac{1}{2} \). The smallest three integers having the same ratio are 2, 3, 3, and thus the indices of the plane are (233).

Figure 18  Indices of some important planes in a cubic crystal. The plane (200) is parallel to (100) and to (100).

Figure 19  A (111) plane of an fcc crystal structure, based on (100) layers. (Photograph by J. F. Nicholas, Atlas of models of crystal surfaces, Gordon and Breach, 1965.)
Miller lattices and directions.

Equivalent faces are designated by curly brackets (braces). Thus the set of cube faces can be represented as \(\{100\}\) in which
\[
\{100\} = (100) + (010) + (001) + (100) + (010) + (001)
\]

Directions: A line is constructed through the origin of the crystal axis in the direction under consideration and the coordinates of a point on the line are determined in multiples of lattice parameters of the unit cell. The indices of the direction are taken as the smallest integers proportional to these coordinates and are closed in square brackets. For example, suppose the coordinates are \(x = 3a, y = b, z = c/2\), then the smallest integers proportional to these three numbers are 6, 2, and 1 and the line has a [621] direction.
Axis system for a hexagonal unit cell (Miller–Bravais scheme).

\[
\begin{align*}
\begin{bmatrix} u' & v' & w' \end{bmatrix} & \longrightarrow \begin{bmatrix} uv & vt & w \end{bmatrix} \\
u & = & \frac{n}{3} \left(2u' - v'\right) \\
v & = & \frac{n}{3} \left(2v' - u'\right) \\
t & = & -(u + v) \\
w & = & nw'
\end{align*}
\]
Figure 1—4
Packing of hard spheres in an fcc lattice.
Packing density.

- Simple cube vs. closed packed.

- The atomic packing factor (APF).

The APF is defined as the fraction of solid sphere volume in a unit cell.

\[
\text{APF} = \frac{\text{volume of atoms in a unit cell}}{\text{total unit cell volume}}
\]

<table>
<thead>
<tr>
<th>Characteristics of Cubic Lattices</th>
<th>Simple</th>
<th>Body-Centered</th>
<th>Face-Centered</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit Cell Volume</td>
<td>(a^3)</td>
<td>(a^3)</td>
<td>(a^3)</td>
</tr>
<tr>
<td>Lattice Points Per Cell</td>
<td>1</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Nearest Neighbor Distance</td>
<td>(a)</td>
<td>(\frac{a\sqrt{3}}{2})</td>
<td>(\frac{a}{\sqrt{2}})</td>
</tr>
<tr>
<td>Number of Nearest Neighbors</td>
<td>6</td>
<td>8</td>
<td>12</td>
</tr>
<tr>
<td>Second Nearest Neighbor Distance</td>
<td>(a\sqrt{2})</td>
<td>(a)</td>
<td>(a)</td>
</tr>
<tr>
<td>Number of Second Neighbors</td>
<td>12</td>
<td>6</td>
<td>6</td>
</tr>
</tbody>
</table>
Packing and interstitial sites.

- Unoccupied interstitial site in the FCC structure: tetragonal and octahedral.
- Unoccupied interstitial site in the BCC structure: interstitial with distorted octahedral and octahedral symmetry.

**FCC**

**BCC**

<table>
<thead>
<tr>
<th>Element</th>
<th>( a ) (nm) (^a)</th>
<th>Element</th>
<th>( a ) (nm) (^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.405</td>
<td>Ca</td>
<td>0.559</td>
</tr>
<tr>
<td>Ni</td>
<td>0.352</td>
<td>Cu</td>
<td>0.361</td>
</tr>
<tr>
<td>Pd</td>
<td>0.389</td>
<td>Ag</td>
<td>0.409</td>
</tr>
<tr>
<td>Ir</td>
<td>0.384</td>
<td>Au</td>
<td>0.408</td>
</tr>
<tr>
<td>Pb</td>
<td>0.495</td>
<td>Yb</td>
<td>0.548</td>
</tr>
</tbody>
</table>

Interstitials are very important in formation of solid solutions. Example: C:Fe steel.
### Packing density and stability of the lattice.

<table>
<thead>
<tr>
<th>Coordination Number</th>
<th>Cation–Anion Radius Ratio</th>
<th>Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>&lt;0.155</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.155–0.225</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.225–0.414</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.414–0.732</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>0.732–1.0</td>
<td></td>
</tr>
</tbody>
</table>

- Instability of Ti is related to a series of successful phase transitions in BaTiO₃.