Crystal Structures

Kittel Chpt 1
Ashcroft + Mermin Chpt 4

In most solids, the ions sit at the sites of a well-defined periodic lattice of points. We now seek to describe this lattice, giving the geometric structure of the lattice of ions.

Bravais lattice - specifies the periodic array in which the units of the crystal are organized. Two equivalent definitions of the Bravais lattice are:

a) An infinite array of discrete points where the arrangement and orientation appears exactly the same from whichever point the array is viewed.

b) A 3-dimensional Bravais lattice consists of all points \( \mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 \)

where \( \mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3 \) are not all in the same plane, and \( n_1, n_2, n_3 \) are any integers.

\( \mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3 \) are called the primitive vectors of the Bravais lattice - they are not unique. (Primitive vectors sometimes called the basis vectors)
An example of a 2-D Bravais lattice with no special symmetry is given by \( \vec{a}_1, \vec{a}_2 \) of different lengths, with a angle \( \theta \neq \frac{2\pi}{n} \) between them.

3D simple cubic lattice \( \vec{a}_1 = a\hat{x}, \vec{a}_2 = a\hat{y}, \vec{a}_3 = a\hat{z} \)

3D Body centered cubic (bcc) take simple cubic and put an extra atom in the center of each cubic cell. Looks like two interpenetrating simple cubic lattices.

Primitive vectors:
\[
\vec{a}_1 = a\hat{x}, \quad \vec{a}_2 = a\hat{y}, \quad \vec{a}_3 = a\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)
\]

or a more symmetric choice:
\[
\vec{a}_1 = \frac{a}{2}(\hat{y}+\hat{z}-\hat{x}), \quad \vec{a}_2 = \frac{a}{2}(\hat{x}+\hat{z}-\hat{y}), \quad \vec{a}_3 = \frac{a}{2}(\hat{x}+\hat{y}-\hat{z})
\]
3D face centered cubic (fcc)

Take a single cubic lattice and add an atom to the center of every face of each cubic cell.

Primitive vectors

\[ \mathbf{a}_1 = \frac{a}{2} (y + \mathbf{g}) \]
\[ \mathbf{a}_2 = \frac{a}{2} (z + \mathbf{x}) \]
\[ \mathbf{a}_3 = \frac{a}{2} (x + y) \]

Bcc and fcc are very common lattice structures. Single cubic is very rare (only \( \alpha \)-phase of polonium under normal conditions).

**fcc:**
- Ar, Ag, Al, Au, Ca, Ce, \( \beta \)-Co, Cu,
- In, Kr, La, Ne, Ni, Pb, Pt, Pr, Pt,
- S-Pu, Rh, Sc, Sr, Th, Xe, Yb
- lattice constant \( a \sim 3-6 \text{ Å} \)

**bcc:**
- Ba, Cr, Cs, Fe, K, Li, Mo, Na, Nb,
- Rb, Ta, Th, V, W
- \( a \sim 3-6 \text{ Å} \)

Brauer lattice - this term can refer to either the set of points, or the set of vectors:

\[ \mathbf{R} = \sum n_i \mathbf{a}_i \]
Coordination number - the number of points in a Bravais lattice that are closest to a given point is the coordination number \( z \). These closest points are the "nearest neighbors" of the given point. Each point has the same coordination number:

- sc. \( z = 6 \)
- b.c.c. \( z = 8 \)
- fcc \( z = 12 \)

**primitive cell** - a volume of space that, when translated by all vectors \( \mathbf{r} \) in the Bravais lattice, will fill all of space without any overlaps or voids.

The primitive cell is not unique just as the choice of primitive vectors \( \mathbf{a}_i \) is not unique.

For a given set of primitive vectors \( \mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3 \), then the volume swept out by the set of points

\[
\mathbf{r} = x_1 \mathbf{a}_1 + x_2 \mathbf{a}_2 + x_3 \mathbf{a}_3
\]

with \( 0 \leq x_i \leq 1 \), is an example of a primitive cell.

Since the primitive cell must contain only one Bravais lattice point, the volume
\( V \) of a primitive cell must be such that
\[
V = N \cdot \frac{V}{N} = \frac{V}{N} \quad N = \text{total number of lattice points}
\]
\[
V = \text{total volume}
\]
\[
\Rightarrow \quad \frac{V}{N} = \frac{1}{m} \quad m = \text{density of lattice points}
\]
\( \frac{V}{N} \) is independent of choice of the primitive cell

The primitive cell need not have the full symmetry of the crystal.

**Unit cell or conventional cell** - a volume that fills up all space without overlaps or voids when translated by some particular subset of vectors of the Bravais lattice.

The unit cell is bigger than the primitive cell, and usually chosen for convenience with the symmetry of the lattice.

For example, for bcc or fcc, one can take as the unit cell the single cubic cell which is decorated to form the bcc or fcc structure. The parameters that specify the size of the unit cell are called the lattice constants.
Wigner-Seitz cell

This is a uniquely defined choice for a primitive cell that has the full symmetry of the Bravais lattice. We define it as follows:

Choose a point \( \mathbf{P} \) in the Bravais lattice. The region of space closer to \( \mathbf{P} \) than to any other point \( \mathbf{P}' \) in the Bravais lattice is the Wigner-Seitz cell.

Since above definition makes no reference to any particular set of primitive vectors, the W-S cell has all the same symmetries of the Bravais lattice.

To construct the W-S cell, draw lines from \( \mathbf{P} \) to all other points \( \mathbf{P}' \) in the Bravais lattice. Bisect each such line with a plane. The inner envelope of these planes is the surface of the W-S cell.

see KIT-AL or AM for W-S cells of 3D BL
Wigner-Seitz cell, when translated through all lattice vectors, will just fill space without overlapping; i.e., the Wigner-Seitz cell is a primitive cell.

Since there is nothing in the definition of the Wigner-Seitz cell that refers to any particular choice of primitive vectors, the Wigner-Seitz cell will be as symmetrical as the Bravais lattice.\(^\text{12}\)

The Wigner-Seitz unit cell is illustrated for a two-dimensional Bravais lattice in Figure 4.14 and for the three-dimensional body-centered cubic and face-centered cubic Bravais lattices in Figures 4.15 and 4.16.

Note that the Wigner-Seitz unit cell about a lattice point can be constructed by drawing lines connecting the point to all others\(^\text{13}\) in the lattice, bisecting each line.

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\(^{12}\) A precise definition of "as symmetrical as" is given in Chapter 7.

\(^{13}\) In practice only a fairly small number of nearby points actually yield planes that bound the cell.
Crystalline Structure - Bravais lattice with a basis

Crystals can form periodic structures which are **not Bravais lattices** - all points are not equivalent, either due to positioning of atoms or because different atoms occupy different sites. Such structures are called a lattice with a basis and are described by an underlying B-L plus a set of basis vectors that give the positions of the atoms with respect to each B-L site R.

**Example**: honeycomb lattice in 2D

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<--- this is not a Bravais lattice!

The ○ sites are all equivalent, but the ● sites are not equivalent to the ○ sites!

Note: ○ sites all have a ● neighbour to the upper right whereas ● sites do not - they have a neighbour to the lower left ●. Hence the orientational environment of ● sites is different from that of ○ sites.
But we can describe the honeycomb lattice as a 2D triangular lattice with a two-point basis. Let the \( \bullet \) sites describe the sites \( \vec{R} \) of a triangular BL.

![Diagram of honeycomb lattice]

Dashed lines show the honeycomb structure. Solid lines show the underlying triangular BL.

**Primitive vectors**

\[
\begin{align*}
\vec{a}_1 &= a \hat{x} \\
\vec{a}_2 &= a \left( \frac{\sqrt{3}}{2} \hat{x} + \frac{\sqrt{3}}{2} \hat{y} \right)
\end{align*}
\]

**Basis vectors**

\[
\begin{align*}
\vec{d}_1 &= 0 \quad \text{gives } \bullet \text{ sites} \\
\vec{d}_2 &= \frac{a}{\sqrt{3}} \hat{y} \quad \text{gives } \circ \text{ sites}
\end{align*}
\]

**Sites of honeycomb lattice given by**

\[
\{ \vec{R} + \vec{d}_1, \vec{R} + \vec{d}_2 \} \quad \text{with } \vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2, \quad n_1, n_2 \text{ integers}
\]
We could describe the fcc and bcc Bravais lattices as single cubic lattices with a basis:

- primitive vectors:
  \[
  \begin{align*}
  \vec{a}_1 &= a\vec{x} \\
  \vec{a}_2 &= a\vec{y} \\
  \vec{a}_3 &= a\vec{z}
  \end{align*}
  \]

- basis vectors bcc:
  \[
  \begin{align*}
  \vec{b}_1 &= 0 \\
  \vec{b}_2 &= \frac{a}{2}(\vec{x}+\vec{y}+\vec{z})
  \end{align*}
  \]

- basis vectors fcc:
  \[
  \begin{align*}
  \vec{c}_1 &= 0 \\
  \vec{c}_2 &= \frac{a}{2}(\vec{x}+\vec{y}) \\
  \vec{c}_3 &= \frac{a}{2}(\vec{y}+\vec{z}) \\
  \vec{c}_4 &= \frac{a}{2}(\vec{z}+\vec{x})
  \end{align*}
  \]

**Diamond Structure**

Two interpenetrating fcc lattices displaced along the body diagonal of the cubic unit cell by 1/4 the length of the diagonal.

(See Ashcroft + Mermin Fig. 4.18)

- fcc Bravais lattice with four point basis:
  \[
  \begin{align*}
  \vec{d}_1 &= 0 \\
  \vec{d}_2 &= \frac{a}{4}(\vec{x}+\vec{y}+\vec{z})
  \end{align*}
  \]

- Coordination number \( z = 4 \) - tetrahedral bonds

Examples: C, Si, Ge, α-Sn
Bonds lengths from atom at \( \bar{r}_1 = \frac{a}{4} (x+y+z) \) to origin and faces are the same.

\[ |\bar{r}_1 - \frac{a}{2} (x+y)| = \left| -\frac{a}{4} x - \frac{a}{4} y + \frac{a}{4} z \right| = \frac{\sqrt{2}}{4} a \]

\[ |\bar{r}_1 - \frac{a}{2} (z+y)| = \left| -\frac{a}{4} x + \frac{a}{4} y - \frac{a}{4} z \right| = \frac{\sqrt{2}}{4} a \]

\[ |\bar{r}_1 - \frac{a}{4} (9+y)| = \left| \frac{a}{2} x - \frac{a}{2} y - \frac{a}{2} z \right| = \frac{\sqrt{2}}{4} a \]

Each atom of diamond structure has 4 equal length bonds to 4 nearest neighbors. These bonds form the edge of a tetrahedron.
Hexagonal close packed

Single hexagonal B-lattice - obtained by stacking 2D triangular lattices directly above each other.

2D triangular lattice

\( \vec{a}_1 = a \hat{x} \)
\( \vec{a}_2 = \frac{a}{2} \hat{x} + \frac{\sqrt{3}}{2} a \hat{y} \)
\( \vec{a}_3 = c \hat{z} \)
all angles 60°

hexagonal close packed -

two interpenetrating single hexagonal Bravais lattices displaced by \( \vec{d}_2 = \frac{\vec{d}_1 + \vec{d}_2 + \vec{d}_3}{3} \)
with \( c = \sqrt{\frac{8}{3}} a = 1.63299 \alpha \)

obtained by close packing of hard spheres

put 2nd layer on

1st layer - then

are two choices how

to do this - one choice
is given by the triangles
as picture on the left.
For the 3rd layer, put the sphere on the "holes" in the 2nd layer, so that they lie directly above the spheres in the 1st layer. This gives the hexagonal close-packed structure.

For each layer, there are always two choices:

\[
\begin{array}{cccccc}
  & \times & \times & \times & \times & \\
  & \times & \times & \times & \times & \\
  & \times & \times & \times & \times & \\
\end{array}
\]

Let \(\bullet\) be sites of 1st layer. Then we can always put next layer down on top of the \(\circ\)'s or the \(\times\)'s.

If put 2nd layer on the \(\circ\)'s, then the 3rd layer can go on either the \(\times\)'s or the \(\bullet\)'s. We can call these three sets of sites \(A, B, C\) (for \(\bullet, \circ, \times\)).

Then the close packing corresponds to the stacking sequence \(ABABAB\ldots\) in the hexagonal closed packed. The stacking sequence \(ABCABCABC\ldots\) turns out to give the face centered cubic lattice!

Certain rare earth crystals have stacking \(ABACABAC\ldots\)

Could in principle make the choice between the two possibilities at each layer randomly. This would give a random close packed structure.
NaCl structure

Space points where atoms sit is a simple cubic Bravais lattice but sites are not equivalent since they are alternately occupied by different atoms (Na and Cl for salt).

Need to describe this as a fcc Bravais lattice with two point basis

\[ \vec{a}_1 = 0, \quad \vec{a}_2 = \frac{a}{2} (x+y+z) \]

- Na at sites of fcc
- Cl at center of cube

(See A+M Fig. 4.24)

Cesium Chloride Structure

Equal numbers of cesium and chlorine at points of a bcc lattice so that each has 8 neighbors of the other kind.

Described by simple cubic Bravais lattice of Cs with Cl at center of unit cube

\[ \vec{a}_1 = 0 \quad \text{Cs} \]
\[ \vec{a}_2 = \frac{a}{2} (x+y+z) \quad \text{Cl} \]

Zincblend Structure equal numbers of zinc and sulfur on a diamond lattice so that each has 4 nearest neighbors of the other type.