Outline

- Crystal Structure
- Band Theory
- Density Functional Theory
- Local Density Functional Approximation
- Band Structure and Density of States
Chapter 1  Crystal Structure

An ideal crystal is constructed by the infinite repetition of identical structure units in space.

Bravais Lattice: specifies the periodic array in which the repeated units of the crystal are arranged. The unit themselves may be single atoms, groups of atoms, molecules, and ions.
A Bravais lattice consists of all points with position vectors \( \mathbf{R} \) of the form

\[
\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3
\]

\( \mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3 : \) primitive vectors

A basis of atoms is attached to every lattice point, with every basis identical in composition, arrangement, and orientation. The position of the center of an atom \( \mathbf{r}_i \) of the basis relative to the associated lattice point is

\[
\mathbf{r}_i = x_1 \mathbf{a}_1 + x_2 \mathbf{a}_2 + x_3 \mathbf{a}_3 \quad \text{where} \quad 0 \leq x_1, x_2, x_3 \leq 1
\]
Example of Bravais lattice

1. Simple cubic lattice

\[ \vec{a}_1 = a\hat{i} \]
\[ \vec{a}_2 = a\hat{j} \]
\[ \vec{a}_3 = a\hat{k} \]

2. Body center cubic lattice

\[ \vec{a}_1 = \frac{a}{2}(-\vec{i} + \vec{j} + \vec{k}) \]
\[ \vec{a}_2 = \frac{a}{2}(\vec{i} - \vec{j} + \vec{k}) \]
\[ \vec{a}_3 = \frac{a}{2}(\vec{i} + \vec{j} - \vec{k}) \]
3. Face centered cubic lattice (fcc)

\[
\bar{a}_1 = \frac{a}{2} (\vec{j} + \vec{k})
\]

\[
\bar{a}_2 = \frac{a}{2} (\vec{i} + \vec{k})
\]

\[
\bar{a}_3 = \frac{a}{2} (\vec{i} + \vec{j})
\]

4. Hexagonal lattice

\[
\bar{a}_1 = a \left( \frac{1}{2} \vec{i} + \frac{\sqrt{3}}{2} \vec{j} \right)
\]

\[
\bar{a}_2 = a \left( \frac{1}{2} \vec{i} - \frac{\sqrt{3}}{2} \vec{j} \right)
\]

\[
\bar{a}_3 = c \vec{k}
\]
Primitive cell

Wigner-Seitz primitive cell

Drawing lines connecting the point to all others in the lattice, bisecting each line with a plane, and taking the smallest polyhedron containing the point bounded by these planes.
Example of Wigner-Seitz primitive cell

Wigner-Seitz primitive cell of bcc lattice

Wigner-Seitz primitive cell of fcc lattice
Table 3  Crystal structures of the elements

The data given are at room temperature for the most common form, or at the stated temperature in deg K. For further descriptions of the elements see Wyckoff, Vol. 1, Chap. 2. Structures labeled complex are described there.
Some examples of crystal structures and lattices with basis

1. Diamond structure
   fcc lattice
   \[ \bar{\tau}_1 = 0 \]
   \[ \bar{\tau}_2 = \frac{1}{4} (\bar{i} + \bar{j} + \bar{k}) \]

2. Zincblende structure
   fcc lattice
   \[ \tilde{\tau}_1 = 0 \]
   \[ \tilde{\tau}_2 = \frac{1}{4} (\tilde{i} + \tilde{j} + \tilde{k}) \]
3. Sodium chloride structure

fcc lattice

\[ \vec{\tau}_1 = 0 \]

\[ \vec{\tau}_2 = \frac{a}{2} \hat{i} \]

NaCl, LiH, MnO, KCl, KBr

4. Cesium chloride structure

sc lattice

\[ \vec{\tau}_1 = 0 \]

\[ \vec{\tau}_2 = \frac{a}{2} (\hat{i} + \hat{j} + \hat{k}) \]

CsCl, AgMg, AlNi, CuPd
5. Hexagonal closed-packed structure (hcp)

hex lattice

\[ \bar{\tau}_1 = 0 \]

\[ \bar{\tau}_2 = \frac{2}{3} \bar{a}_1 + \frac{1}{3} \bar{a}_2 + \frac{1}{2} \bar{a}_3 \]

hcp: ABABABABAB……

fcc: ABCABCABC…….

c \cong 1.633a

fcc along (111) direction
Reciprocal lattice

\[ \vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3 \]
\[ \vec{a}_1, \vec{a}_2, \vec{a}_3 : \text{primitive vectors} \]

\[ \vec{G} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3 \]
\[ \vec{b}_1, \vec{b}_2, \vec{b}_3 : \text{reciprocal lattice vectors} \]

\[ \vec{a}_i \cdot \vec{b}_j = 2\pi \delta_{ij} \]

\[ e^{i\vec{G} \cdot (\vec{r} + \vec{R})} = e^{i\vec{G} \cdot \vec{r}} \]

\[ \therefore \vec{G} \cdot \vec{R} = 2\pi (n_1 h + n_2 k + n_3 l) \]

The set of all wave vector \( \vec{G} \) that yield plane waves with the periodicity of a given Bravais lattice is known as its reciprocal lattice.

The reciprocal lattice vectors is given by:

\[ \vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} \quad ; \quad \vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} \quad ; \quad \vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} \]

First Brillouin zone (1BZ) : the Wigner-Seitz primitive cell of the reciprocal lattice
1. Simple cubic lattice (sc)

\[
\vec{a}_1 = a\hat{i} \\
\vec{a}_2 = a\hat{j} \\
\vec{a}_3 = a\hat{k}
\]

\[
\vec{b}_1 = \frac{2\pi}{a}\hat{i} \\
\vec{b}_2 = \frac{2\pi}{a}\hat{j} \\
\vec{b}_3 = \frac{2\pi}{a}\hat{k}
\]

The reciprocal lattice of a sc lattice is a sc lattice of side \(\frac{2\pi}{a}\).

2. Body center cubic lattice (bcc)

\[
\vec{a}_1 = \frac{a}{2}(-\vec{i} + \vec{j} + \vec{k}) \\
\vec{a}_2 = \frac{a}{2}(\vec{i} - \vec{j} + \vec{k}) \\
\vec{a}_3 = \frac{a}{2}(\vec{i} + \vec{j} - \vec{k})
\]

\[
\vec{b}_1 = \frac{4\pi}{a}\frac{1}{2}(\vec{j} + \vec{k}) \\
\vec{b}_2 = \frac{4\pi}{a}\frac{1}{2}(\vec{i} + \vec{k}) \\
\vec{b}_3 = \frac{4\pi}{a}\frac{1}{2}(\vec{i} + \vec{j})
\]

The reciprocal lattice of a bcc lattice is a fcc lattice of side \(\frac{4\pi}{a}\).
3. Face centered cubic lattice (fcc)

\[
\bar{a}_1 = \frac{a}{2} \left( \bar{j} + \bar{k} \right) \\
\bar{a}_2 = \frac{a}{2} \left( \bar{i} + \bar{k} \right) \\
\bar{a}_3 = \frac{a}{2} \left( \bar{i} + \bar{j} \right)
\]

\[
\bar{b}_1 = \frac{4\pi}{a} \left( -\bar{i} + \bar{j} + \bar{k} \right) \\
\bar{b}_2 = \frac{4\pi}{a} \left( \bar{i} - \bar{j} + \bar{k} \right) \\
\bar{b}_3 = \frac{4\pi}{a} \left( \bar{i} + \bar{j} - \bar{k} \right)
\]

The reciprocal lattice of a fcc lattice is a bcc lattice of side \( \frac{4\pi}{a} \)

4. Hexagonal lattice (hex)

\[
\bar{a}_1 = a \left( \frac{1}{2} \bar{i} + \frac{\sqrt{3}}{2} \bar{j} \right) \\
\bar{a}_2 = a \left( \frac{1}{2} \bar{i} - \frac{\sqrt{3}}{2} \bar{j} \right) \\
\bar{a}_3 = c\bar{k}
\]

Homework: \( \bar{b}_1, \bar{b}_2, \bar{b}_3 = ? \)