LATTICES

Symmetry

and all that
LATTICES & SYMMETRY

Ch. 3 m6 & 4k.

Crystal and broken symmetry:

New phases

In general the hamiltonian:

$$H = \frac{1}{2m} \sum_{i=1}^{N} p_i^2 + \sum_{i<j} V(r_i - r_j)$$

is invariant under:

- Translation: \( \bar{r}_i \rightarrow \bar{r}_i + \tilde{\delta} \)
- Rotation: \( \bar{r}_i \rightarrow R \bar{r}_i \)
- Space inversion: \( \bar{r} \rightarrow -\bar{r} \equiv -(r - R) \)

Are these symmetries present in? 

Liquid

Solid
The state of X%AL is LESS symmetric!

And symmetry is spontaneously broken (see a movie of a milk droplet)

Note crystallization happens the particles arrange themselves into special positions to minimize energy.

For specifics of symmetry breaking, read pp 21-24 MC & KY.

Bravais lattices: simplest

B.L. is a mathematical object with desired symmetries

B.L. is a set of points span by:

$$\vec{R}_n = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$$

$n_2$ is an integer #.

$$[\vec{a}_1, \vec{a}_2, \vec{a}_3] = \text{primitive lattice vectors}$$
**Simple Cubic**

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

- These are **NOT** atoms!

**Face-Centered Cubic (FCC)**

\[ \mathbf{a}_1 = \left( \frac{\mathbf{a}}{2} \right) \left( \mathbf{y} + \mathbf{z} \right), \quad \mathbf{a}_2 = \left( \frac{\mathbf{a}}{2} \right) \left( \mathbf{x} + \mathbf{z} \right), \quad \mathbf{a}_3 = \frac{\mathbf{a}}{2} \left( \mathbf{x} + \mathbf{y} \right) \]

- As you can see, FCC and BCC can be obtained by decorating **simple cubic**.

**Body-Centered Cubic (BCC)**

\[ \mathbf{\bar{a}}_1 = \frac{\mathbf{a}}{2} \left( \mathbf{y} + \mathbf{z} - \mathbf{x} \right), \quad \mathbf{\bar{a}}_2 = \frac{\mathbf{a}}{2} \left( \mathbf{z} + \mathbf{x} - \mathbf{y} \right), \quad \mathbf{\bar{a}}_3 = \frac{\mathbf{a}}{2} \left( \mathbf{x} + \mathbf{y} - \mathbf{z} \right) \]

- All added points are the same as the original ones, but new primitive vectors are required.

- # of nearest neighbors is called the **coordination number** = 12
e.g. SC has $z = 6$

FCC $z = 12$

BCC $z = 8$

in the periodic table FCC and BCC are the most common

Larger coordination = greater stability

Q: What element(s) has SC lattice?

Another way to describe B. lattice is to specify its primitive unit cell (p.u.c.) with a fixed shape which when translated by primitive vectors entirely fills up crystalline space without voids.
- p.u.c. is a better idea as atoms, ions etc. are not point-like.

- Electron w.f. spreads over xtal and the whole u.c.

- p.u.c. is not unique

\[ \text{Wigner - Seitz cell} = \]

\[ = \text{Special kind of p.u.c.} \]

Mathematically it is defined as:

\[
\mathbf{r} - \text{inside W} \rightarrow \text{p.u.c.} \\
1 \leq 1 - \mathbf{r} - \mathbf{R}_n \Rightarrow \\
\mathbf{r}^2 < \mathbf{r}^2 - 2 \mathbf{r} \cdot \mathbf{R}_n + \mathbf{R}_n \cdot \mathbf{R}_n \\
\Rightarrow (\mathbf{r} - \frac{\mathbf{R}_n}{2}) \cdot \mathbf{R}_n < 0
\]

- Boundaries of W are planes bisecting lattice vectors

- W cell has full point symmetry of the B.L. (i.e. a set of point symmetry transform which leaves the xtal invariant)
w.z. p.u.c. for 2D square lattice $|\vec{a}_1| = |\vec{a}_2| = a$.

The shape of w.z. and the primitive lattice is not always the same (most often!), e.g.

or non primitive u.c.

triangular lattice p.u.c.

w.z. p.u.c.
In general there are more than 1 atom per u.c.

\[ \vec{R}_{\text{h},s} = \vec{R}_{\text{h}} + \vec{e}_s \quad s = 1, 2, \ldots, m \]

- we attach a set of $m$ inequivalent points to sites of a B.L.

We call those = lattice with bases

c.e.g. Graphene:

\[ \vec{a}_1 \text{ and } \vec{a}_2 = \text{primitive vectors} \]

\[ \tau \text{ is NOT a primitive vector} \]

(\(A \not\equiv B\) are inequivalent atoms)

B.L. triangular lattice with 2 point basis
What kind of lattice would you assign?
Figure 1.3 (a) Body-centered cubic lattice, showing generators of cubic and alternative (Bravais) unit cells. (b) Wigner-Seitz cell.

Figure 1.4 (a) Face-centered cubic lattice, showing cubic and alternative (Bravais) unit cells. (b) Wigner-Seitz cell.
- e.g. graphene, diamond, Silicon, and Germanium
  - all 2 atom per u.c.
  - b/c. those are simple elements
  - those 2-atoms are the same.

Introduction to VESTA software

- what's this lattice (tet)
- ζ is along diagonal of the cube
  with 1/4 of diagonal length.

\[ \vec{\zeta} = \frac{a}{4} (x + \sqrt{2}y + \sqrt{2}z) \]

(often called)

↓

Diamond
- Diamond is a 3D generalization of graphene.

- Δ lattice \( z = 6 \)
  it can be tiled as
  \[ \square \]
  with lattice sites at the vertices.

- B sites sit at the center of each A triangle, and so is A ... \( \Rightarrow \) honeycomb lattice has coordination \( z = 3 \)

- Similarly FCC lattice \( z = 12 \)
  can be tiled from regular tetrahedra, with 2 different directions.

- In diamond sublattice the 2nd sublatt.
  is in the center of 1st tetrahedron.
A diamond lattice has $Z = 4$.

Q: Why do you think those 3D xtalr have such low $Z$?

A (hint): Consider $C^\text{ion} = 4$ valent $e^-$ which form 4 bonds e.g. in graphene.
NaCl: simple cubic 01
Each u.c. contains Na+ and Cl-
and B.L. is FCC

Zinc Blend: ZnS

is diamond lattice with
2 types of atom sitting
in opposite corners:
other examples: GaAs, AlAs
-they cannot form a B.L. as
each u.c. contains more than
one atom.
Conventional u.c. (c.u.c) 12

c.u.c. contains more than one lattice site but has a simple geometrical shape

\[ V_{c.u.c} = n V_{p.u.c} \]

\# of lattice sites in the c.u.c.

E.g. we could use Cubic c.c.c. for bcc or fcc.

Symmetry

- Translation symmetry is broken spontaneously to map crystal into itself:
- Rotation: by $2\pi/n$
  axis are $n$-fold axis of rotation

- Reflection about a plane (in 2D - line)

- Inversion about a special point - called an inversion center
  (in 2D an inversion = $\pi$ rotation around an inversion center)

- Combination of all is a symmetry group
By specifying the symmetries of crystals in 3D can be classified in 32 groups. (for more see Ashcroft & Mermin)

**Reciprocal Lattice**

Recall F.T. is a great way to describe periodic functions:

\[ p(\vec{R}) = p(\vec{R} + \vec{R}_n) \]

Let's construct the lattice like this:

\[ p(\vec{R}) = \sum_{n_1, n_2, n_3} f(\vec{R} - n_1 \vec{a}_1 - n_2 \vec{a}_2 - n_3 \vec{a}_3) \]

Electron density of basis atoms inside one u.c.
\[ FT: \quad \rho(R) = \frac{1}{\sqrt{16\pi}} e^{iG \cdot \vec{R}} \]

by demanding that
\[ \rho(R) = \rho(R + R_n) \]
\[ e^{iG \cdot (\vec{R} + n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3)} = e^{iG \cdot \vec{R}} \implies e^{iG \cdot R_n} = 1 \]

\[ \Rightarrow \quad G \cdot \vec{a}_j = 2\pi m_j, \quad j = 1, 2, 3 \]

set of 3 eqns. \quad m = 0, 1, 2, \ldots 

The set of such 6 vectors also forms a B.L. in a
Momentum Space \equiv \text{Reciprocal Space}
Example:

\[ b_1 = \frac{2\pi}{a_1}, \quad b_1 = \frac{2\pi}{a_2} \]

Let's check:

\[ b_1 \cdot a_1 = 2\pi \]
\[ b_1 \cdot a_2 = 0 \]
\[ b_2 \cdot a_1 = 0 \]
\[ b_2 \cdot a_2 = 2\pi \]

Hence

\[ \vec{c} = m_1 \vec{b}_1 + m_2 \vec{b}_2 \]

Since it satisfies:

\[ \vec{c} \cdot \hat{a}_j = 2\pi m_j \]

But often R.L. is not the same type as direct lattice.
e.g. for 2D:

\[ b_i = \epsilon_{ij} \left( \hat{z} \times \hat{a}_j \right) \]

where \( \hat{z} \) is a unit vector along the normal direction of the lattice plane and

\[ \epsilon_{ij} = -\epsilon_{ji} \]

anti-symmetric Levi-Civita

\[ \epsilon_{12} = -\epsilon_{21} = 1 \]

\[ \epsilon_{11} = \epsilon_{22} = 0 \]

\[ \Rightarrow \bar{a}_m \cdot \bar{b}_j = \delta_{mj} \cdot 2\pi \]

W.z. cell of the reciprocal space is the 1st B. Z. Brillouin zone
Now in 3D:

\[ \omega = \bar{a}_1 \cdot (a_2 \times a_3) \]

\[ \Rightarrow \text{a volume of p.u.c.} \]

Let's define:

\[ b_1 = \frac{2\pi}{\omega} a_2 \times a_3 \]

\[ b_2 = \frac{2\pi}{\omega} a_3 \times a_1 \]

\[ b_3 = \frac{2\pi}{\omega} a_1 \times a_2 \]

\[ \bar{b}_j = \frac{1}{2} \frac{2\pi}{\omega} \epsilon_{jkl} e \cdot (\bar{a}_k \times \bar{a}_l) \]

and \( \bar{a}_m \cdot \bar{b}_j = 2\pi \delta_{m,j} \)
1st B.Z. of common structures

(a) fcc
(b) bcc
(c) hcp

Figure 1.18 Brillouin zones for the fcc, bcc, and hcp structures.

The capital Latin & Greek letters are some important high symmetry points.
Recall $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ etc.

Now we can think of any 3D lattices as a set of 2D lattices made of plane of atoms $\mathbf{K} \sim \mathbf{G}$

So we can label this set of lattice planes by this r. e. vector

$e.g. \quad \mathbf{G}_{klm} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$

From math: a plane is defined by a point and a vector $\perp$ to the plane $\mathbf{G}_{klm} \cdot \mathbf{r} = 0$

(Notice often we use $h,k,l$)
As $\mathbf{G} \cdot \mathbf{R}_j = 2\pi n_j$ for all lattice points, there exist a set of parallel planes of atoms so that

$$\mathbf{G}_{KLM} \cdot \mathbf{r} = 0, \pm 2\pi, \pm 4\pi, \ldots$$

Those planes are labeled by their MILLER INDICES (b.t.w. I assume that $\mathbf{G}$ is the shortest vector to the plane).

We can find M.I.'s in the real space:

$$\mathbf{R}_{n_1n_2n_3} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$$

So $\mathbf{G}_{KLM} \cdot \mathbf{R}_{n_1n_2n_3} = (K_{n_1} + 2n_2 + M_{n_3}) \cdot 2\pi = 2\pi I$

$I$ is some integer fixed.
Let's set $h_2 = h_3 = 0$ we solve for $h_1$,

$$
\frac{1}{h_1} = \frac{I}{K}
$$

$$
\frac{1}{h_2} = \frac{I}{L}
$$

$$
\frac{1}{h_3} = \frac{I}{M}
$$

$$
\Rightarrow (K, L, M) = \left(\frac{I}{h_1}, \frac{I}{h_2}, \frac{I}{h_3}\right)
$$

Consider examples:

A direction normal to a plane with Miller indices $(hkl)$ is labeled as $[hkl]$

This a line passing through the point with coordinate $(hkl)$ if the intercept is negative we say $(hkl)$

Figure 1.13 Plane specified by the Miller indices $(hkl)$. 
Alternatively, if we have 3 numbers intersecting axes the Miller-Ind. is the SMALLEST integer of \( \frac{1}{h_1} : \frac{1}{h_2} : \frac{1}{h_3} \).

\( \frac{1}{2} : \frac{1}{2} : \frac{1}{2} \) or \( 2:2:2 \) => \( \frac{1}{2} : \frac{1}{2} : 1 \) or \( 2:2:6 \) =

so the M.I. is \( (2 \ 2 \ 6) \). More examples:

**Figure 1.14** Miller indices of major symmetry planes of the bcc lattice.

**Figure 1.15** Miller indices of major symmetry planes of the bcc lattice.
Common reciprocal lattice

\[ \begin{align*}
(100) & : z = \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \\
(110) & : z = \frac{1}{3}, \frac{1}{3}, \frac{1}{3} \\
(111) & : z = \frac{1}{4}, \frac{1}{4}, \frac{1}{4}
\end{align*} \]

**M.I. for planes in cubic lattice**

**Real Space**

**Reciprocal Space**

**Dispersion Relation**

\[
d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}
\]

**Example**

\[ a = 3.61 \text{ Å} \quad (220) \]

\[ d_{220} = \frac{0.361}{\sqrt{2 \cdot 2 \cdot 0}} = 0.128 \text{ nm} = 1.28 \text{ Å} \]
Example: Let's compute some interesting numbers for NaCl.

NaCl crystallizes in a cubic structure.

Molecular weight of NaCl = 56.46 \( \frac{g}{\text{mole}} \)

\[ 22.989 + 35.453 \]

and density at R.T. \( 2.167 \frac{g}{cm^3} \)

Q: What is the lattice constant of NaCl?

\[
M_{\text{NaCl molecule}} = 58.46 \frac{g}{\text{mole}} \cdot \frac{1}{6.02 \times 10^{23} \text{mol}} = 9.7 \times 10^{-23} g.
\]

\[
\frac{\# \text{ of NaCl}}{\text{Unit Volume}} = 2.167 \frac{g}{cm^3} \cdot \frac{\# \text{Molecule}}{9.7 \times 10^{-23} g} = 2.23 \times 10^{22} \text{ molecules/cm}^3
\]
b/c NaCl is diatomic

\[
\frac{\text{# of atoms}}{\text{Volume}} = \frac{2 \text{ atoms}}{\text{molecule}} \cdot \frac{22 \text{ g}}{\text{mol}} \cdot \frac{1 \text{ mol}}{2.23 \cdot 10^{24} \text{ cm}^3} = 4.5 \cdot 10^{22} \text{ atoms/cm}^3
\]

Let \( a \) to be distance measured along the edge of the cube

\( h \) = number of atoms along the edge of 1 cm x 1 cm x 1 cm cube

\[
L_{\text{edge}} = h \cdot a \quad \Rightarrow \quad V = h^3 a^3
\]

\[
h^3 = \# \text{ atoms in 1 cm}^3 \quad \Rightarrow \\
4.5 \cdot 10^{22} \cdot a^3 = 1 \quad \Rightarrow \\
a = 2.82 \cdot 10^{-8} = 2.82 \text{ Å}
\]
Next we can calculate spacing between crystal lattices:

Figure 1.16 Spacing between crystal planes in cubic lattice.

As you can see, $d_{100} = \text{lattice constant}$

$$d_{110} = \frac{d_{100}}{\sqrt{2}} = 1.99 \text{ Å}$$

and

$$d_{111} = \frac{d_{100}}{\sqrt{3}} = 1.63 \text{ Å}$$
Recall in the Born approx.

$$\frac{d\sigma}{d\Omega} \sim |F(q)|^2$$

with $q = \mathbf{k} - \mathbf{k}'$

at $T=0k$: $f(r) = \sum \rho_a(r-R_a)$

Sum of sites inside underlying Br. lattice
and $\rho_a$ - atomic density

$$\Rightarrow F(q) = \int d^3r e^{-i\mathbf{q}\cdot\mathbf{r}} \sum \rho_a(r-R_a)$$

$$\Rightarrow F(q) = w_c(q) \cdot f(q) = \Sigma e^{i\mathbf{q}\cdot\mathbf{R}}$$
Figure 6.18  Diffraction-pattern intensities explained using the convolution theorem. (a) An infinite crystal can be thought of as the convolution of the electronic distribution within the unit cell with the Bravais lattice. (b) Using the convolution theorem, it becomes apparent that the diffraction pattern is the product of the FT of the electronic distribution in the unit cell (called the ‘structure factor’) and the FT of the Bravais lattice, which, like the Bravais lattice itself, is another infinite 3D comb function (see text).
Let's go back to our original discussion:

\[ p(r) = \sum_i p_\alpha(r - \mathbf{r}_i) \Rightarrow \]

\[ F(q) = \int d^3r \ e^{-i \mathbf{q} \cdot \mathbf{r}} \sum_i p_\alpha(r - \mathbf{r}_i) \]

\[ = \sum_i e^{-i \mathbf{q} \cdot \mathbf{r}_i} \]

Now notice if \( \mathbf{q} = \mathbf{k} - \mathbf{k}' \) is not an element of \( G \) (recipr. latt.):

\[ \Rightarrow w = 0 \]

if however \( \mathbf{q} = \mathbf{0} \)

then \( e^{-i \mathbf{G} \cdot \mathbf{r}_i} = 1 \Rightarrow w \to \infty \)

\[ w(q) = \sum_{l,m,n} e^{-i \mathbf{q} \cdot (a_l \mathbf{e}_l + a_m \mathbf{e}_m + a_n \mathbf{e}_n)} \]

\[ = N \sum_\delta \delta_{q, \delta} \text{ or by using Poisson summation} \]

\[ \sum_{l,m} \frac{(2\pi)^3 \delta(2\pi k - \mathbf{q} \cdot \mathbf{a}_l) \delta(2\pi l - \mathbf{q} \cdot \mathbf{a}_2)}{\delta(2\pi M - \mathbf{q} \cdot \mathbf{a}_3)} = \frac{1}{a_1 \cdot (a_2 \times a_3)} \geq (2\pi)^3 \delta(q - \delta) \]

Finally:

\[ F(q) = f(q) \frac{(2\pi)^3}{V} \geq \delta^3 \delta(q \cdot \delta) \]
How scattering pattern depends on # of scatterers?

Simple view of diffraction - optics like

\[ n d = 2 d \sin \theta \]

Integer # of \( \lambda \)'s into the optical path difference results in interference

If we express: \( \chi = \frac{h c}{\lambda} \)

\[ \sin \theta = \frac{6.1998}{\chi} \]

\( d_{\text{hk}l} \equiv \text{spacing between scatt. planes} \)

C\(_{2}\)(PO\(_{4}\))\(_{3}\) with Lab Cu K\(_{\alpha}\) source
But it all was about the lattice (basis) symmetry.

\[
Q = 2k_1 \sin \theta = \frac{\sqrt{3}}{\pi} \sin \theta
\]

If \( k = 1 \) and \( k = 6 \), i.e., the reciprocal lattice ends in the diffraction maximum, \( F(q) = 0 \).

X-ray scattering of intensity you see, no scattered with random phases, \( E(\theta) \). 1. When you are random...
Periodic functions and geometric structure factor.

A generalization of multiply periodic function:

\[ \rho (r + R_n) = \rho (r) \]

where \( \rho (r) = \sum_{\alpha=0}^{s-1} \delta (r - R_n - \tau_\alpha) \)

E.g. for Cu-Zn alloy we take \( \tau_0 = 0 \) to be the coordinate of Cu atom (in bcc cubic) and \( \tau = \frac{1}{2} \xi (1,1,1) \) for Z atoms.

or for BaTiO\(_3\) - the most famous ferroelectric

\[ \tau_1 = \frac{1}{2} \xi (1,1,1) \]

and \( \tau_2 = \frac{1}{2} \xi (1,0,0) \)

\[ \beta\text{-brass} = \text{Cu-Zn alloy} \]

[Diagrams of Cu-Zn and BaTiO\(_3\) structures]
Based on the result
\[ F(q) = w(q) \cdot f(q) \]
we can say that BCC faces are bounded by planes whose M.I. are such that \( w(q) \neq 0 \).

E.g., consider f.c.c. cubic structure with 4 base atoms:

Atoms located at \( \bar{r}_0 = (0, 0, 0) \)
\( \bar{r}_1 = a \left( \frac{1}{2}, \frac{1}{2}, 0 \right) \)
\( \bar{r}_2 = a \left( 0, \frac{1}{2}, \frac{1}{2} \right) \)
\( \bar{r}_3 = a \left( \frac{1}{2}, 0, \frac{1}{2} \right) \)

From this \( w(q) \) or often labeled as \( S(q) \):
\[
\frac{1}{\# \text{atoms}} \sum_\text{within u.c.} \frac{1}{\# \text{atm}} \sum_i \mathbf{b}_i \cdot \mathbf{T}_m
\]
where
\[
\mathbf{b} = \sum \mathbf{r}_i \mathbf{b}_i \quad \text{and} \quad \mathbf{b}_i \cdot \mathbf{a}_j = 2\pi \delta_{ij}.
for b.c.c.:

\[
\begin{align*}
    a'_1 &= \frac{1}{2} a \quad (1 \ 1 \ -1) \\
    a'_2 &= \frac{1}{2} a \quad (-1 \ 1 \ 1) \\
    a'_3 &= \frac{1}{2} a \quad (1 \ -1 \ 1) \\
\end{align*}
\]

atomic coordinates are expressed as fraction of basis vectors

Latin per u.c. with \( a' \) primitive vectors:

From this set of \( a' \) we can generate the set of reciprocal vectors \( b_i' \):

\[
    b_i' \cdot a'_j = 2\pi \delta_{i,j} \quad \Rightarrow \quad b_i' = \frac{2\pi (a'_j \times a'_k)}{a'_i \cdot (a'_k \times a'_j)}
\]

\[
    = \frac{1}{2} a^3
\]

\( i, j, k = 1, 2, 3 \)

or

\[
\begin{align*}
    \vec{b}_1' &= \frac{2\pi (a'_2 \times a'_3')}{\frac{1}{2} a^3} = \frac{2\pi}{a} \left( \begin{array}{c} 1/2 \\ 1/2 \\ 0 \end{array} \right) \\
    \vec{b}_2' &= \frac{2\pi (a'_3 \times a'_1')}{\frac{1}{2} a^3} = \frac{2\pi}{a} \left( \begin{array}{c} 0 \\ 1/2 \\ 1/2 \end{array} \right) \\
    \vec{b}_3' &= \frac{2\pi (a'_1 \times a'_2')}{\frac{1}{2} a^3} = \frac{2\pi}{a} \left( \begin{array}{c} 1/2 \\ 0 \\ 1 \end{array} \right)
\end{align*}
\]

\[
\sum_{i} \vec{g} \cdot \vec{b}_i' = \Rightarrow \quad \overline{g} \cdot \overline{z} = \left( h_1 \overline{b}_1 + h_2 \overline{b}_2 + h_3 \overline{b}_3 \right)
\]

\[
\left( \overline{v}_0 + \overline{v}_1 + \overline{v}_2 + \overline{v}_3 \right) = \Rightarrow
\]
Now recall: very generally

Atomic coordinates

\[ \hat{r}_m = x_m \hat{a}_1 + y_m \hat{a}_2 + z_m \hat{a}_3 \]

= \( (x_m, y_m, z_m) \)

Reciprocal Lattice vectors:

RLV

\[ \mathbf{G} = h \hat{b}_1 + k \hat{b}_2 + l \hat{b}_3 = (h, k, l) \]

\[ \implies \mathbf{G} \cdot \hat{r}_m = h x_m + k y_m + l z_m \]

and hence

\[ F(h, k, l) = \sum_{m \text{ atoms}}^{} e^{2\pi i \mathbf{G} \cdot \hat{r}_m} \]

\[ = \sum_{m \text{ atoms}}^{} e^{2\pi i (hx_m + ky_m + lz_m)} \]

Let's practice:
Cubic lattice - simple:

basis: \( a_1 = a \hat{x} \), \( a_2 = a \hat{y} \), \( a_3 = a \hat{z} \)

Let's assume we have 2 basis atoms.

\( f_A \) \( \tau_1 = (0, 0, 0) \)

\( f_B \) \( \tau_2 = (x, y, z) \)

Calculate

\[ F(hk1) = \]
BCC with 2 basis atoms

\[ \tau_1 = (0, 0, 0) \]
\[ \tau_2 = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \]
\[ f_1 = f \]
\[ f_2 = f \]

\[ F(hk1) = \ldots ? \]
FCC with 4 atoms basis

\[ \tau_1 (0, 0, 0) \]
\[ \tau_2 (0, \frac{1}{2}, \frac{1}{2}) \]
\[ \tau_3 (\frac{1}{2}, 0, \frac{1}{2}) \]
\[ \tau_4 (\frac{1}{2}, \frac{1}{2}, 0) \]

\[ F(h k l) = \]
**Summary:**

Figure 6.13  Allowed reflections as a function $h^2 + k^2 + l^2$ for the four unit cell types simple cubic (sc), body-centred cubic (bcc), face-centred cubic (fcc), and diamond. Notice that no reflections exist even in principle if $h^2 + k^2 + l^2 = 8m - 1$, where $m$ is an integer greater or equal to unity (shown here in red font). The repeat pattern unit for each cell type is highlighted in yellow.

**Convolution theorem**

\[
\hat{f}(u) = f(x) \ast g(x) = \int f(x) g(u-x) \, dx
\]

Also,

\[
f(x) \ast g(x) \leftrightarrow F(u) G(u)
\]
### Allowed list of $h^2 + k^2 + l^2$ for cubic crystals

<table>
<thead>
<tr>
<th>Forbidden numbers</th>
<th>Primitive, P</th>
<th>Face Centered, F</th>
<th>Body Centered, I</th>
<th>Corresponding $hkl$</th>
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<td>100</td>
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If the observed $\sin^2(\theta)$ follows in a ratio of 1, 2, 3, 4, 5, 6, 8, ..., then the unit cell is likely **primitive cubic**. The common factor is $\lambda^2/4a^2$.

---

*Let’s do real "experiment"*

**Indexing Example – SrTiO$_3$**

- **Perovskite**
- **Quantum paraelectric**

![X-ray diffraction pattern of SrTiO$_3$](image)
Using Bragg's Law, $\lambda = 2d_{hk\ell} \sin \theta$

<table>
<thead>
<tr>
<th>Peak #</th>
<th>$2\theta$ ($^\circ$)</th>
<th>$\theta$ ($^\circ$)</th>
<th>d (Å)</th>
<th>$1/d^2$</th>
<th>$(1/d^2)/Z$</th>
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<tbody>
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<td>1</td>
<td>22.72</td>
<td>11.36</td>
<td>3.910</td>
<td>0.0654</td>
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</tr>
<tr>
<td>2</td>
<td>32.56</td>
<td>16.28</td>
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</table>

$\sin^2 \theta_{hk\ell} = \left( \frac{h^2 + k^2 + l^2}{a^2} \right)^2 (h^2 + k^2 + l^2)$

Note that in this example, we obtain all integers and all the quotients are integers that indicate a primitive unit cell.

**Assignment of Miller indices**

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</table>

The (300) and (221) peaks fall at the same location, both give $h^2 + k^2 + l^2 = 9$.

$$\lambda = \frac{2a \sin(\theta)}{\sqrt{(h^2 + k^2 + l^2)}}$$

The lattice parameter, $a$, is 3.91 Å
Diffraction of electrons

1927 Davisson & Germer showed $e^-$ also diffract.

Now you know that brightness of the Bragg spot is defined by the number of factors, e.g.

X-ray: electron density at the lattice sites

$e^-$ beam: potential energy of $e^-$ in the field of the lattice of atoms.

$+ T$ of xtal and roughness of surface

and of course the geometrical structure factor $s(c)$

**Electron scattering form factor**

$$u(r) \propto u(r+1)$$

$$u(r) = \sum_{\text{basis atoms}} \frac{1}{\alpha} \left( r - R_n \right)$$

$r$: lattice sites

We can measure $\theta(\theta, \varphi)$ given by the scattering rate into the interval $d \kappa = \kappa^2 \sin \theta \, d \theta \, d \varphi$ per unit time.
According to the Fermi Golden rule 2

\[
R_{K \rightarrow K'} = \frac{2\pi}{\hbar} \sum_{K'} |\langle K' | V | K \rangle|^2 \delta(E_{K'} - E_K)
\]

\[\uparrow\text{summed over the final state momenta}\]

Now let's introduce the beam energy per \( e^- \) \( E = \frac{\hbar^2 k^2}{2m} \) and assuming that \( k'=k \) and \( d\Sigma = \sin \theta d\theta d\phi \) we can write down:

\[
\sigma(\theta, \phi) \frac{dE}{d\Sigma} = \frac{2\pi |\langle k' | V | k \rangle|^2}{\hbar} \left( \frac{dE}{\hbar k'} \right)^2
\]

\[
= \frac{2\pi}{\hbar} \left( \frac{|\langle k' | V | k \rangle|^2}{\hbar k} \right)
\]

Consider

\[
\langle k' | V | k \rangle = \frac{1}{\sqrt{N}} \int dr e^{-ik'r} V(r) e^{i\mathbf{k}' \cdot \mathbf{r}}
\]

\[\uparrow\text{integrate over } \mathbf{r}\]

\[\int dr e^{-i(k'-k)' \cdot r} \sum_{n} (r - \mathbf{k}_n - \mathbf{r}_n) = \sum_{l} \mathbf{S}_l(\mathbf{r}) \cdot \mathbf{w}_{\mathbf{c}l}(\mathbf{r}) \text{ with } q = k - k',\]

\[\uparrow\text{geometric structure factor} \]
where \( \psi(q) \) as for x-rays

\[
\text{volume of } x + t + l. \quad \text{is F.T. of the potential}
\]

So for electrons

e.g. if a free \( \varepsilon \) scatters off \( tk \) \( \Theta \)

\[
\psi(r) = \begin{cases} 
- \psi & r \leq R \\
0 & r > R 
\end{cases}
\]

\[
U(q) = \frac{1}{V_0} \int dr \ e^{iqr} \psi(r) = \int_0^R \frac{\sin qr}{qr} \ r^2 \ dr
\]

\[
= - \frac{4\pi U}{V_0} \frac{1}{q^3} \ (\sin qR - qR \cos qR)
\]

where \( q = 2\pi \sin \theta = \frac{4\pi \sin \theta}{\lambda} \)

Figure 2.7 Geometry for elastic electron scattering.

**THE END OF LECTURE**