Chapter 2 X-ray diffraction and reciprocal lattice

I.   Waves

1.   A plane wave is described as
$$\Psi(x,t) = A\, e^{i(\mathbf{k}\cdot\mathbf{x}-\omega t)}$$
A is the amplitude, k is the wave vector, and $\omega=2\pi f$ is the angular frequency.

2.   The wave is traveling along the **k** direction with a velocity c given by $\omega=c|\mathbf{k}|$. Wavelength along the traveling direction is given by $|k|=2\pi/\lambda$.

3.   When a wave interacts with the crystal, the plane wave will be scattered by the atoms in a crystal and each atom will act like a point source (Huygens' principle).

4.   This formulation can be applied to any waves, like electromagnetic waves and crystal vibration waves; this also includes particles like electrons, photons, and neutrons. A particular case is X-ray. For this reason, what we learn in X-ray diffraction can be applied in a similar manner to other cases.

II.   X-ray diffraction in real space – Bragg's Law

1.   A crystal structure has lattice and a basis. X-ray diffraction is a convolution of two: diffraction by the lattice points and diffraction by the basis. We will consider diffraction by the lattice points first. The basis serves as a modification to the fact that the lattice point is not a perfect point source (because of the basis).

2.   If each lattice point acts like a coherent point source, each lattice plane will act like a mirror.
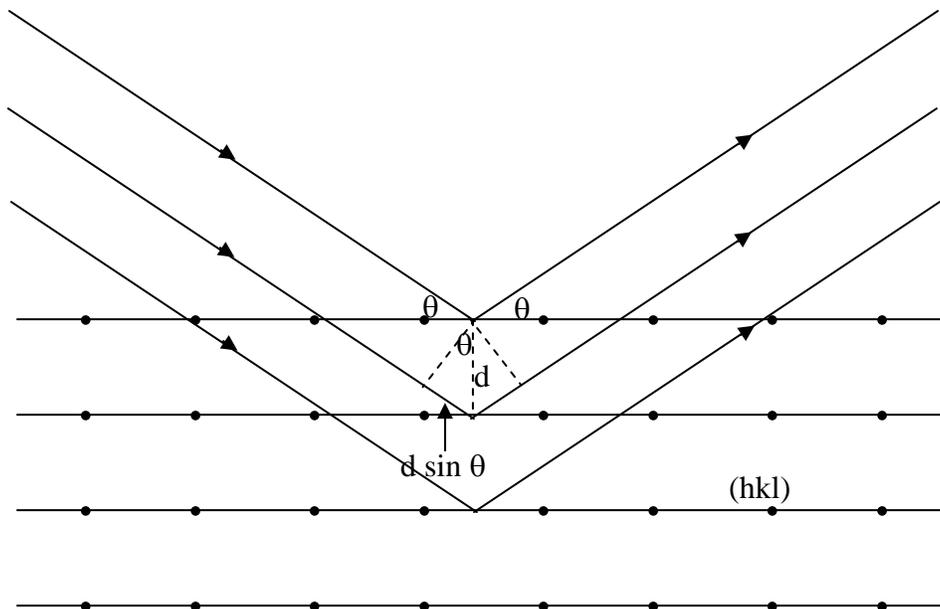
2.   The diffraction is *elastic*. In other words, the X-rays have the same frequency (hence wavelength and |$\mathbf{k}$|) before and after the reflection.

3.   Path difference between two consecutive planes is 2d sin θ, where d is the distance between the planes. For first order constructive interference,

$$2d \sin \theta = \lambda \qquad \text{(Bragg's Law)}$$

Higher order diffraction is possible. In this case, the peaks will be labeled as (nh,nk,nl).

II.   Fourier transformation of crystal and reciprocal lattice vectors

1.   Define reciprocal lattice *primitive* vectors $\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$ as:

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{V} \qquad \vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{V} \qquad \vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{V}$$

where V is the volume of a primitive cell, $V = \vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3$

2.   Relationship between real space primitive vector $\mathbf{a}$ and reciprocal space primitive vector $\mathbf{b}$:

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij}$$

3.   Can generate reciprocal lattice G:
$$\mathbf{G} = l\,\mathbf{b}_1 + m\,\mathbf{b}_2 + n\,\mathbf{b}_3 \quad \text{(l, m, n are any ingtegers)}$$

4.   In general, the longer is $\mathbf{a}$, the shorter is $\mathbf{b}$. That's why $\mathbf{b}$ is called the reciprocal (primitive) vector.

5. $$e^{i\vec{G}\cdot\vec{R}} = e^{i(l\vec{b}_1 + m\vec{b}_2 + n\vec{b}_3)\cdot(l'\vec{a}_1 + m'\vec{a}_2 + n'\vec{a}_3)} = e^{i2\pi(ll' + mm' + nn')} = 1$$

$e^{i\mathbf{G}\cdot\mathbf{r}}$ has the same periodicity of the crystal because $e^{i\mathbf{G}\cdot(\mathbf{r}+\mathbf{R})} = e^{i\mathbf{G}\cdot\mathbf{r}}\, e^{i\mathbf{G}\cdot\mathbf{R}} = e^{i\mathbf{G}\cdot\mathbf{r}}$.

6.   Since $e^{i\mathbf{G}\cdot\mathbf{r}}$ has the same periodicity as the crystal, $\int_{Cell} e^{i\vec{G}\cdot\vec{r}}dV$ should have a value independent on the choice of the cell. Suppose we translate the cell through a vector $\mathbf{d}$,

$$\int_{Cell} e^{i\vec{G}\cdot(\vec{r}+\vec{d})}dV = \int_{Cell} e^{i\vec{G}\cdot\vec{r}}dV \Rightarrow (e^{i\vec{G}\cdot\vec{d}} - 1)\int_{Cell} e^{i\vec{G}\cdot\vec{r}}dV = 0$$

$$\Rightarrow \int_{Cell} e^{i\vec{G}\cdot\vec{r}}dV = 0 \text{ if } \vec{G} \neq 0$$

$$\text{If } \vec{G} = 0, \int_{Cell} e^{i\vec{G}\cdot\vec{r}}dV = \int_{Cell} dV = V$$

$$\therefore \int_{Cell} e^{i\vec{G}\cdot\vec{r}}dV = V\delta_{\vec{G},0}$$

7.   Important:
The set of functions {$e^{i\mathbf{G}\cdot\mathbf{r}}$, $\mathbf{G} = l\,\mathbf{b}_1 + m\,\mathbf{b}_2 + n\,\mathbf{b}_3$} form a complete, orthonormal set for any periodic function Ψ($\mathbf{r}$) following the same periodicity of the crystal Ψ($\mathbf{r}$)= Ψ($\mathbf{r}$+$\mathbf{R}$).

$$\Psi(\vec{r}) = \sum_{\vec{G}} A_{\vec{G}}\, e^{i\vec{G}\cdot\vec{r}}$$

This is the "Fourier transformation" of the periodic function $\Psi(\mathbf{r})$.

8.   We can do the inverse Fourier transformation to find $A_{\mathbf{G}}$:

$$\Psi(\bar{r}) = \sum_{\bar{G}} A_{\bar{G}}\, e^{i\bar{G}\cdot\bar{r}} \Rightarrow \int \Psi(\bar{r})\, e^{-i\bar{G}'\cdot\bar{r}}dV = \sum_{\bar{G}} A_{\bar{G}} \int e^{i\bar{G}\cdot\bar{r}} e^{-i\bar{G}'\cdot\bar{r}}dV$$

$$\Rightarrow \int \Psi(\bar{r})\, e^{-i\bar{G}'\cdot\bar{r}}dV = \sum_{\bar{G}} A_{\bar{G}} \int e^{i(\bar{G}-\bar{G}')\cdot\bar{r}}dV$$

$$\Rightarrow \int \Psi(\bar{r})\, e^{-i\bar{G}'\cdot\bar{r}}dV = \sum_{\bar{G}} A_{\bar{G}}\, V\delta_{\bar{G}\bar{G}'}$$

$$\Rightarrow \int \Psi(\bar{r})\, e^{-i\bar{G}'\cdot\bar{r}}dV = VA_{\bar{G}'}$$

$$\therefore A_{\bar{G}} = \frac{1}{V}\int \Psi(\bar{r})\, e^{-i\bar{G}\cdot\bar{r}}dV$$

III.   Condition of diffraction in terms of reciprocal lattice vector G.

1.   Consider two lattice points.
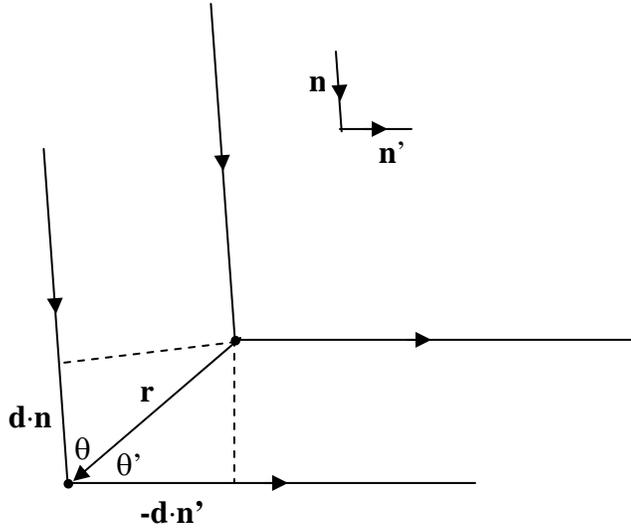
For constructive interference,

$$\bar{r}\cdot\hat{n} - \bar{r}\cdot\hat{n}' \; = \; m\lambda \qquad \text{(order m)}$$

$$\Rightarrow \bar{r}\cdot(\hat{n}-\hat{n}') \; = \; m\lambda$$

$$\Rightarrow \bar{r}\cdot(\bar{k}-\bar{k}') \; = \; 2m\pi$$

2.	Extend above to a lattice, we can replace **r** with a lattice vector R. Therefore the condition for diffraction is given as

$$\mathbf{R}\cdot(\mathbf{k}\text{-}\mathbf{k'}) = 2m\pi$$

From the properties of reciprocal lattice vector, we know that

$$\boxed{\mathbf{k}\text{-}\mathbf{k'} =\mathbf{G}}$$

With $\Delta\mathbf{k} = \mathbf{k'}\text{-}\mathbf{k}$, we have

$$\Delta\mathbf{k} = \mathbf{G} \qquad\qquad (\text{-}\mathbf{G}\rightarrow\mathbf{G})$$

3.	Laue condition

$$\mathbf{k}\text{-}\mathbf{k'} = \text{-}\mathbf{G} \quad\Rightarrow\quad \mathbf{k'} = \mathbf{k}+\mathbf{G}$$
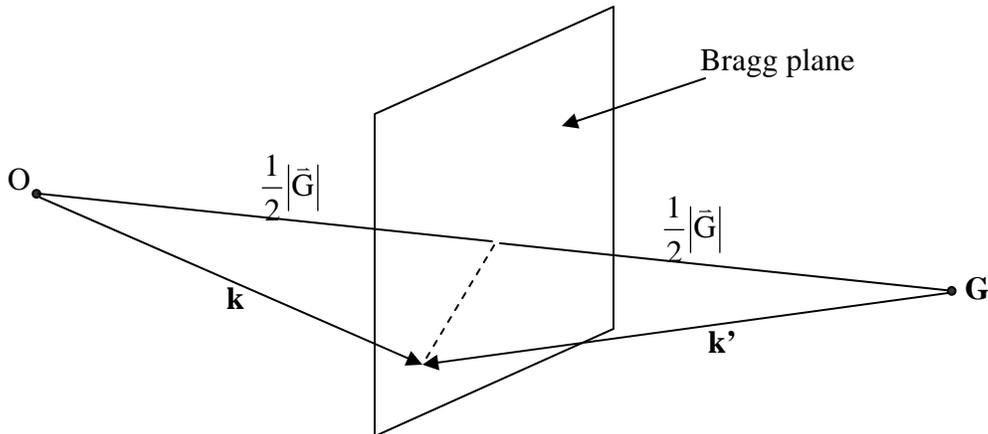$$\Rightarrow\ k'^2=k^2+G^2+2\mathbf{k}\cdot\mathbf{G}$$

For elastic scattering, $|\mathbf{k'}|=|\mathbf{k}| \Rightarrow k'^2=k^2$. Therefore:

$$G^2+2\mathbf{k}\cdot\mathbf{G} = 0 \ \ ,\ \text{or}$$

$$\vec{k}\cdot\hat{G} = \frac{1}{2}\left|\vec{G}\right| \qquad\qquad ,\ \hat{G}\ \text{is a unit vector along the}\ \vec{G}\ \text{direction}$$

This is known as the Laue condition for elastic X-ray diffraction.

4.	Geometric interpretation of Laue condition:

	In other words, diffraction (constructive interference) is the strongest at the perpendicular bisecting plane (Bragg plane) between two reciprocal lattice points. *This is true for any type of waves inside a crystal, including electrons.* Note that in the original real lattice, these perpendicular bisecting planes are the planes we use to construct Wigner-Seitz cell.
	This interpretation is especially useful if the wave has all different **k** and you want which of these **k**'s will be diffracted by the crystal. This is the case for the electrons inside the crystal.
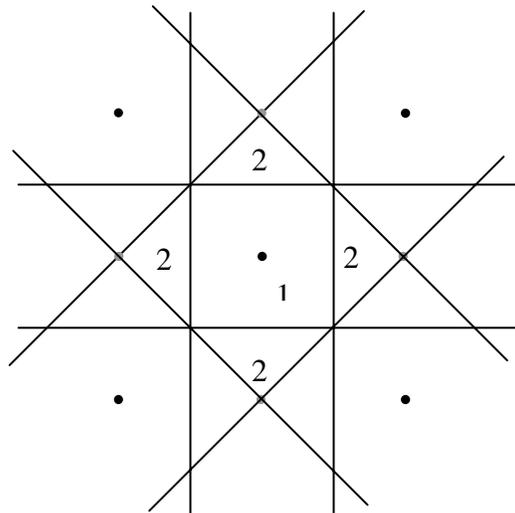
IV.	Brillouin zones

1.   Following the Laue condition, it is important to determine all the perpendicular bisecting planes in the reciprocal lattice. For the neighbors nearest to the origin, this is just the Wigner-Seitz cell of the reciprocal lattice and called the first Brillouin zone.
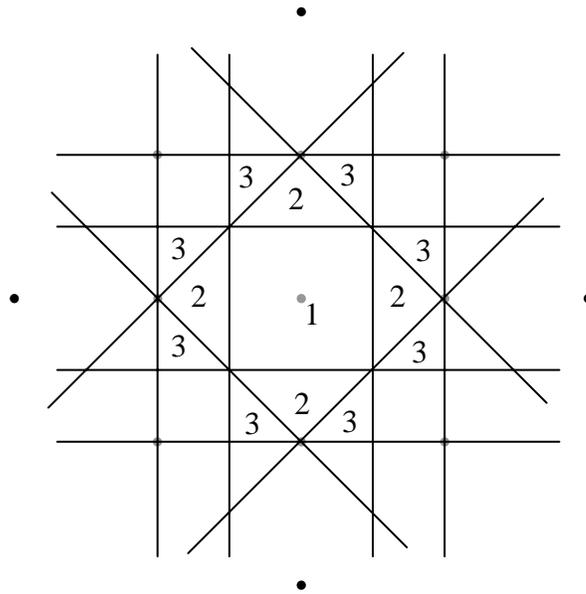
2.   Example:

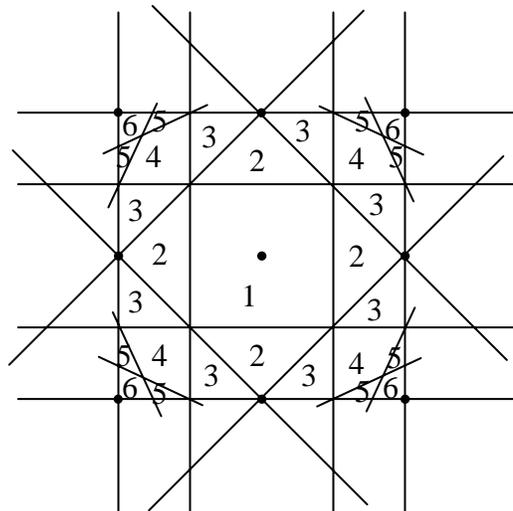First Brillouin zone:
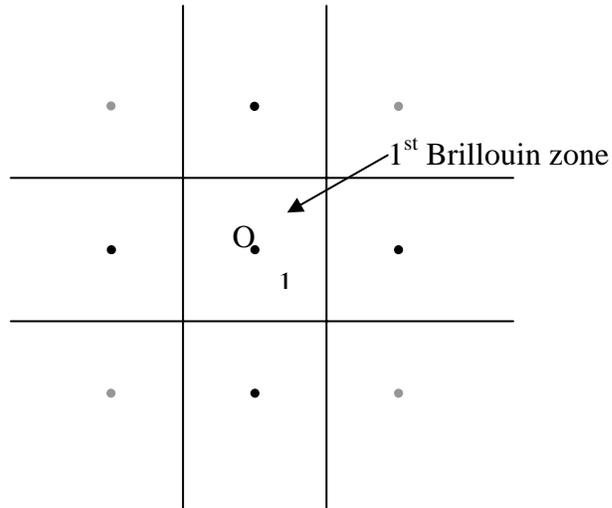
Second Brillouin zone:

Third Brillouin zone:

Higher Brillouin zones:

3.   The first Brillouin zone is the set of points in the reciprocal space that can be reached from the origin without crossing any Bragg plane. The (n+1)th Brillouin zone is the set of points that can be reached from the origin by crossing n-1 Bragg planes, but no fewer.

4.   The Bragg planes enclosing the nth Brillouin zone correspond to the nth order diffraction.

5.   The higher order the Brillouin zone, the more the zone is fragmented. However, in all cases, if we translate these fragments according to the crystal symmetry, they will all look like the first Brillouin zone (this process is called reduced zone scheme).

V.   X-ray refraction of the basis.

1.   We first assume the Laue condition is satisfied. Inclusion of basis means the assumption of point sources at the lattice points have to be modified.

2.   Scattering within the basis:
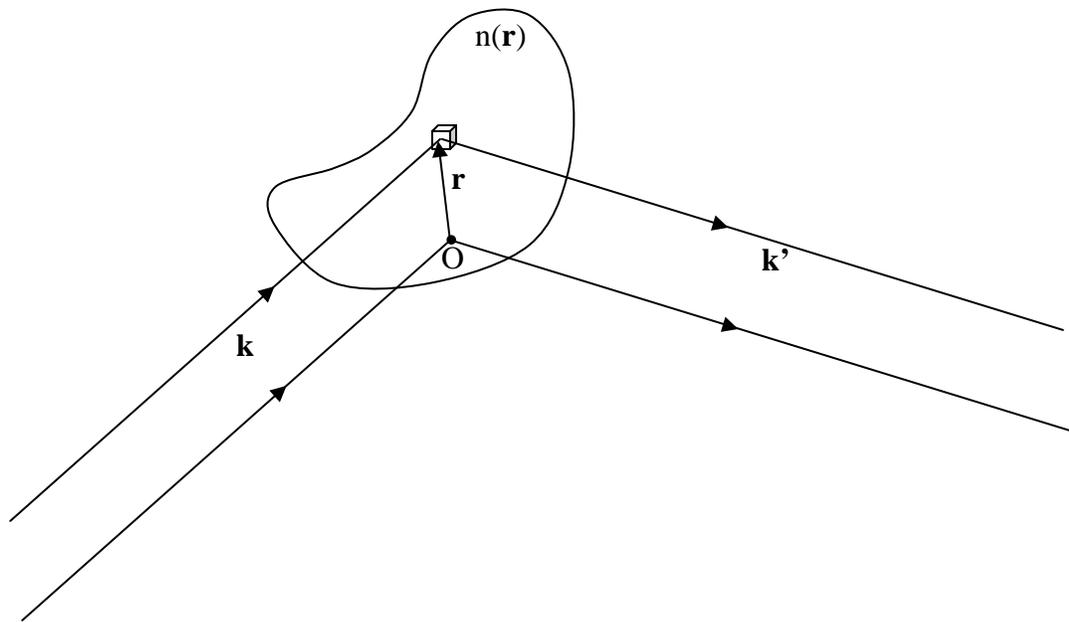
Scattering (i.e. intensity of the diffracted ray) by the infinitesimal element depends on:
    (i)   electron density n($\mathbf{r}$) at the location of the infinitesimal element, and
    (ii)   the phase difference (=($\mathbf{k}$-$\mathbf{k}$')·$\mathbf{r}$) with respect to diffracted ray at the origin.
Therefore we can define *scattering amplitude* (proportional to the amplitude of the oscillation of electric or magnetic field of the *total* diffracted ray) as:

$$F = N \int dV\, n(\vec{r})\, e^{i(k-k')\cdot\vec{r}} \qquad (N = \text{total number of lattice points})$$

3.   Since we are considering only the case of constructive interference for the lattice, i.e. **k-k'=G**. We can also limit the above integration to within the cell. Hence the scattering amplitude becomes:

$$F = N \int_{\text{Cell}} dV\, n(\vec{r})\, e^{-i\vec{G}\cdot\vec{r}} = N S_G$$

$$S_G = \int_{\text{Cell}} dV\, n(\vec{r})\, e^{-i\vec{G}\cdot\vec{r}}$$

S_G is called the *structure factor*.

4.   Suppose there are s atoms in the basis and the positions of these atoms are given by **r**$_j$ (j=1, 2, …, s). We can now write the total electron density n(**r**) as superposition of electron concentration functions n$_j$ associated with each atom j in the basis:

$$n(\vec{r}) = \sum_{j=1}^{s} n_j(\vec{r} - \vec{r}_j)$$

And the scattering amplitude (or the structure factor) can be written as

$$S_G = \int_{\text{Cell}} dV \left[\sum_{j=1}^{s} n_j(\vec{r} - \vec{r}_j) \right] e^{-i\vec{G}\cdot\vec{r}}$$

$$= \int_{\text{Cell}} dV \left[\sum_{j=1}^{s} n_j(\vec{\rho}) \right] e^{-i\vec{G}\cdot\vec{\rho}} e^{-i\vec{G}\cdot\vec{r}_j} \qquad (\vec{\rho} = \vec{r} - \vec{r}_j)$$

$$= \sum_{j=1}^{s} e^{-i\vec{G}\cdot\vec{r}_j} \cdot \int_{\text{Cell}} dV\, n_j(\vec{\rho})\, e^{-i\vec{G}\cdot\vec{\rho}}$$

$$= \sum_{j=1}^{s} f_j e^{-i\vec{G}\cdot\vec{r}_j}$$

$$f_j = \int_{\text{Cell}} dV\, n_j(\vec{\rho})\, e^{-i\vec{G}\cdot\vec{\rho}}$$

f$_j$ is called *atomic form factor*, depends only on the type of element that atom belongs to.

5.   In summary, the total scattering amplitude is given by:

Total scattering amplitude = Scattering amplitude of lattice

$$\times \text{structural factor of basis } S_G \left(= \sum_{j=1}^{s} f_j e^{-i\vec{G}\cdot\vec{r}_j} \right)$$

If there is only one lattice point in the basis, then S_G=1 ($e^{-iG\cdot R}$=1).

6. Example:

Consider bcc as simple cubic with a basis at $\{0, (1/2,1/2,1/2)\}$

Primitive lattice vector for simple cubic are

$$\bar{a}_1 = a\,\hat{i},\; \bar{a}_2 = a\,\hat{j},\; \bar{a}_3 = a\,\hat{k}$$

Therefore the primitive reciprocal lattice vectors are

$$\bar{b}_1 = 2\pi\frac{a^2\,\hat{j}\times\hat{k}}{a^3} = \frac{2\pi}{a}\hat{i} \qquad \bar{b}_2 = 2\pi\frac{a^2\,\hat{k}\times\hat{i}}{a^3} = \frac{2\pi}{a}\hat{j} \qquad \bar{b}_3 = 2\pi\frac{a^2\,\hat{i}\times\hat{j}}{a^3} = \frac{2\pi}{a}\hat{k}$$

Consider the diffraction peak (hkl) (with respect to the simple cubic lattice),

$$G = h\bar{b}_1 + k\,\bar{b}_2 + l\,\bar{b}_3 = \frac{2\pi}{a}(h\,\hat{i} + k\,\hat{j} + l\,\hat{k})$$

$$S_G(hkl) = \sum_{j=1}^{2} f_j e^{-i\bar{G}\cdot\bar{r}_j} = f_1 e^{-ia(h\hat{i}+k\hat{j}+l\hat{k})\cdot\bar{0}} + f_2 e^{-i\frac{2\pi}{a}(h\hat{i}+k\hat{j}+l\hat{k})\cdot\frac{a}{2}(\hat{i}+\hat{j}+\hat{k})}$$

$$= f_1 + f_2 e^{-i\pi(h+k+l)}$$

The bcc diffraction intensity will be the one from simple cubic times $S_G^*(hkl)\,S_G(hkl)$.

$$S_G^*(hkl)\,S_G(hkl) = \left(f_1^* + f_2^* e^{i\pi(h+k+l)}\right)\left(f_1 + f_2 e^{-i\pi(h+k+l)}\right)$$

$$= f_1^2 + f_2^2 + 2\mathrm{Re}[f_1 f_2 e^{-i\pi(h+k+l)}]$$

For particular case, $f_1 = f_2 = f$

$$S_G^*(hkl)\,S_G(hkl) = 2f^2[1 + e^{-i\pi(h+k+l)}] = \begin{cases} 4f^2 & \text{if } h+k+l = \text{even} \\ 0 & \text{if } h+k+l = \text{odd} \end{cases}$$

For bcc structure with the same type of atoms, the (hkl) peaks of the simple cubic will disapper whenever $h+k+l = \text{odd}$.