

Fourier analysis of the basis:

The scattering amplitude which is previously defined as

$F = \int n(\vec{r})e^{-i\Delta\vec{k}\cdot\vec{r}} dV$ can be determined for a crystal of N cells when

the diffraction condition $\Delta\vec{k} = \vec{G}$ is met such that $F_G = NF$:

$$F_G = N \int n(\vec{r})e^{-i\Delta\vec{k}\cdot\vec{r}} dV .$$

When the structure factor is defined as $S_G = \int_{cell} n(\vec{r})e^{-i\vec{G}\cdot\vec{r}} dV$, then

$$F_G = NS_G.$$

The electron concentration $n(\vec{r})$ is defined as $n(\vec{r}) = \sum_{j=1}^s n_j(\vec{r} - \vec{r}_j)$,

where n_j is the electron concentration associated with atom "j" of the cell. The position vector of the atom "j" is \vec{r}_j . While the contribution of atom "j" to the electron concentration at \vec{r} is $n_j(\vec{r} - \vec{r}_j)$ and s represents the total atoms of the basis.

Now S_G can be rewritten as:

$$S_G = \sum_j \int n_j(\vec{r} - \vec{r}_j)e^{-i\vec{G}\cdot\vec{r}} dV$$

Making the change of variable such that $\vec{\rho} = \vec{r} - \vec{r}_j$, the structure factor S_G has the expression:

$$S_G = \sum_j e^{-i\vec{G}\cdot\vec{r}_j} \int n_j(\vec{\rho})e^{-i\vec{G}\cdot\vec{\rho}} dV .$$

Now we can define the atomic form factor with an integral extended over all space as:

$$f_j = \int n_j(\vec{\rho})e^{-i\vec{G}\cdot\vec{\rho}} dV .$$

Thus $S_G = \sum_j f_j e^{-i\vec{G}\cdot\vec{r}_j}$, where $\vec{r}_j = x_j\vec{a}_1 + y_j\vec{a}_2 + z_j\vec{a}_3$ is the position of the center of an atom "j" of the basis relative to the associated lattice point. The origin (called the associated lattice point) can be chosen such that $0 \leq x_j, y_j$ and $z_j \leq 1$.

Then for the reflection labeled by h, k, ℓ we have

$$S_G = \sum_j f_j e^{-i2\pi(hx_j + ky_j + \ell z_j)}, \text{ which is a complex quantity.}$$

The intensity of scattered wave is simply defined by $I_s = S_G^* S_G$.

Important note:

The electrons do not occupy discrete locations $\vec{r}_1, \vec{r}_2, \vec{r}_3 \dots$ etc., but have a continuous charge cloud over the volume of the atom. Thus the concentration of electrons in an atom is taken as the density of cloud $n(\vec{r})$.

The atomic form factor (f_j):

The quantity f_j is a measure of the scattering power of the j^{th} atom in the unit cell. Its value involves:

- 1) The number and distribution of atomic electrons.
- 2) The wave length and angle of scattering radiation.

The scattered radiation from a single atom represents the resulting interference of scattering radiation from all electrons within an atom. The form factor can also be obtained when the integration is extended over electron concentration associated with a single atom and it has the expression:

$$f_j = \int n_j(\vec{r}) e^{-i\vec{G}\cdot\vec{r}} dV$$

The atomic form factor with spherical symmetric electron charge distribution:

Consider an angle α between the reciprocal vector \vec{G} and the position vector \vec{r} at which the electron charge concentration is determined such that $\vec{G} \cdot \vec{r} = Gr \cos \alpha$. Since the electron distribution is taken to be spherically symmetric about the origin, then

$$f_j = \int_0^{2\pi} d\phi \int_0^R r^2 n_j(r) dr \int_0^\pi \sin \alpha e^{-iGr \cos \alpha} d\alpha .$$

Put $\cos \alpha = x \Rightarrow dx = -i \sin \alpha d\alpha$, thus x has the limits between 1 and -1 corresponds to limits of α between 0 and π .

$$f_j = -2\pi \int_0^R r^2 n_j(r) dr \int_1^{-1} e^{-iGrx} dx ,$$

$$f_j = 4\pi \int_0^R r^2 n_j(r) \frac{e^{iGr} - e^{-iGr}}{Gr} dr ,$$

Or
$$f_j = 4\pi \int_0^R n_j(r) r^2 g(Gr) dr ,$$

where $g(Gr) = \frac{\sin Gr}{Gr}$ and R is the radius of the atom. The behavior of the atomic form factor can be deduced when we plot the function $g(Gr)$ versus Gr as shown in figure 38.

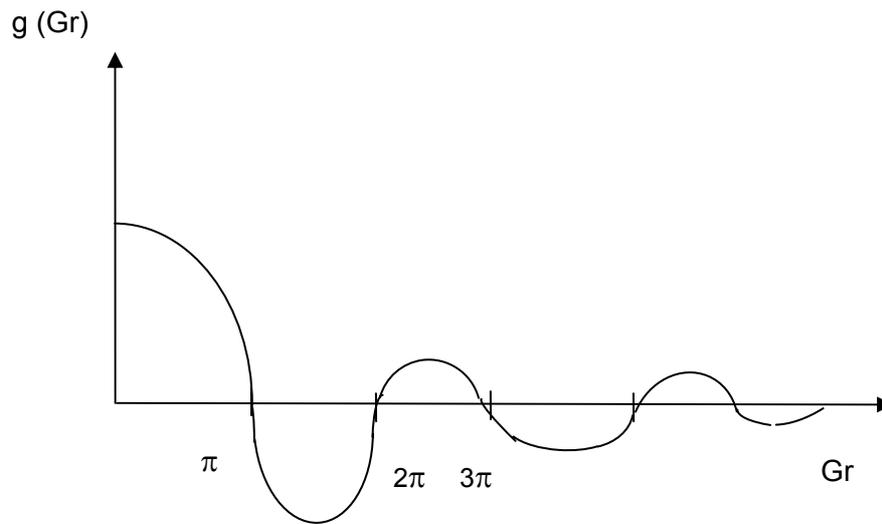


Figure 38: The function $g(Gr)$ versus Gr .

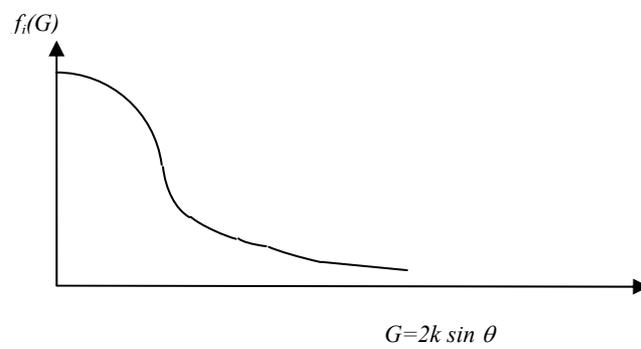


Figure 39: The atomic form factor for a uniform spherical distribution of cloud of electrons.

Conclusions and Remarks:

- i) Since $G = \Delta k = 2k \sin \theta$, then f_j depends on the scattering angle 2θ . So as θ increases G increases and then f_j decrease.
- ii) The wave length is inversely proportional to G i.e. the shorter wave length corresponds to the smaller f_j .
- iii) If the wavelength λ is much greater than the interatomic spacing, then a diffraction pattern is not produced. Thus the atomic form factors and then the need to get a diffraction pattern may put limits on the range of wavelengths used. For example, in the case of carbon atom, when $G = \Delta k = 0$, $\Rightarrow \frac{\sin Gr}{Gr} \rightarrow 1$.

$$f_j(G=0) = \int_0^R 4\pi r^2 n(r) dr \Rightarrow f_j(G=0) = Z = 6, \text{ as shown in figure}$$

39, (where this number represents the total number of electrons in carbon atom).

Exercise:

The number density of the hydrogen atom in its ground state is

given by $n(r) = \frac{e^{-2r/a_0}}{\pi a_0^3}$, where a_0 is the Bohr radius. Show that the

$$\text{form factor is } f_G = \frac{16}{(4 + G^2 a_0^2)^2}$$

The structure factor of a diatomic basis in a crystal:

$$S_G = \sum_{j=1}^2 f_j e^{-2\pi i(hx_j + ky_j + lz_j)}.$$

Thus $S_G = f_1 e^{-i\phi_1} + f_2 e^{-i\phi_2}$, where

$$\phi_1 = 2\pi(hx_1 + ky_1 + lz_1) \text{ and } \phi_2 = 2\pi(hx_2 + ky_2 + lz_2).$$

Note: Identical atoms have identical form factors no matter where they are located.

Structure factor of the bcc lattice:

When the atoms of the bcc basis are identical where one is located at $(x_1, y_1, z_1) \equiv (0, 0, 0)$ and the other at $(x_2, y_2, z_2) \equiv (1/2, 1/2, 1/2)$, the scattering amplitude can be expressed in terms of S_G as:

$$S_G(hkl) = f(1 + e^{-i\pi(h+k+\ell)}), \text{ where } f \text{ is the form factor of an atom.}$$

Question: Can you tell whether the peak intensities can be observed by x-ray diffraction for the planes (100), (111), (210), (200), (110) and (222) or not?

Answer:

$S_G = 0$ when $h + k + \ell =$ odd integer. Thus no peaks appear with the planes (100), (111) and (210). However when $h + k + \ell =$ even integer, then $S_G = 2f$ and pronounced peaks appear with the planes (200), (110) and (222).

Important notes:

- Since both atoms of the basis of bcc structures have the same atomic form factor f , the structure factor is found by using a simple cubic lattice.
- The peak intensities of the fcc and bcc structures are usually indexed using simple cubic lattice vectors.
- All atoms of the non-primitive basis must be included in the structure factor.

Exercise: Use the primitive lattice vectors $\vec{a}_1 = a\hat{x}$, $\vec{a}_2 = a\hat{y}$, $\vec{a}_3 = a\hat{z}$ to determine the structure factor for $CsCl$ structure.