

Study Material - Sem. 5 - C12T -

- Crystal Structure - Dr. T. Kar-

Class 5

Atomic Scattering Factor / Form Factor

The Bragg or Laue equations give the condition for diffraction from point scattering centres (or the point electrons) arranged on a space lattice. But when we are concerned with the intensity of scattering from actual crystals, which are composed of atoms arranged on a lattice, then we must take into account ^{the fact} that the scattering is actually done by the cloud of electrons which surrounds the nuclei. Neglecting the scattering effect of the atomic nuclei, one might expect that the total scattering from an atom would simply be scattering from one electron multiplied by the number of electrons in the atom. This is, however, not the case, since the size of the atom is a X-ray wavelength and therefore,

② all parts of the atom do not scatter in phase to produce the above expected scattering. In fact, the amplitude of the radiation scattered from the atom is only f times of that from a single electron, or in other words —

$$f = \frac{\text{Amplitude of radiation scattered from the atom}}{\text{Amplitude of radiation scattered from an electron.}}$$

The factor ' f ' is called the atomic scattering factor or form factor. Its value is usually less than the number of electrons ' Z ' in the atom. It measures the efficiency with which the atom scatters the incident radiation.

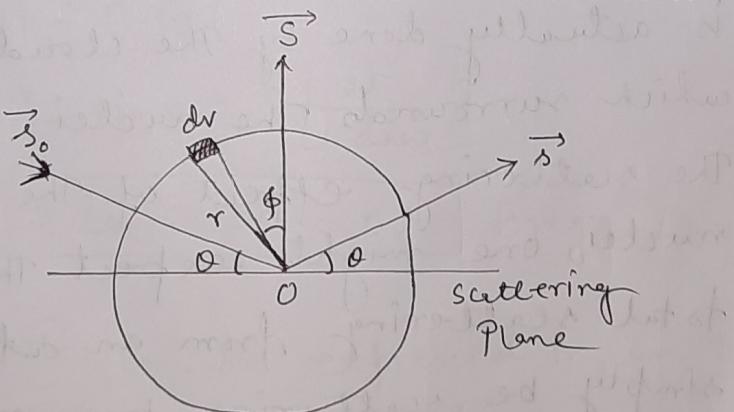


Fig. 1.

Let $f(\vec{r})dv$ be the element of charge located at the volume element dv about the point \vec{r} , (with origin taken at

(3)

The centre of the atom) [fig. 1]. $f(\vec{r})$ is the charge density at point \vec{r} . If \vec{s}_0 be the unit vector in the direction of incident radiation and \vec{s} be the unit vector in the direction of scattered beam, Then the phase difference between the radiation scattered from origin and that scattered from the element $d\mathbf{v}$ is

$$\phi = \frac{2\pi}{\lambda} (\vec{r} \cdot \vec{s}), \quad \vec{s} \rightarrow \text{scattering normal}$$

Let the scattering amplitude from the point electrons at origin in the direction of \vec{s} is $A e^{i(kn - \omega t)}$, where n is the distance coordinate along \vec{s} and $k = \frac{2\pi}{\lambda}$. Then the scattering amplitude from the volume element $d\mathbf{v}$ is —

$$A e^{i(kn - \omega t)} + i\phi f(r) d\mathbf{v}$$

The ratio of the amplitude of the scattered radiation by the element $d\mathbf{v}$ to that by a point electron at origin

$$= df = \frac{A e^{i(kn - \omega t)} + i\phi f(r) d\mathbf{v}}{A e^{i(kn - \omega t)}}$$

$$= f(r) e^{i\phi} d\mathbf{v}$$

(4)

Therefore, the ratio of the scattered amplitude from the whole atom to that from a single electron is —

$$f = \int f(r) e^{i\phi} dr \rightarrow (1)$$

If the distribution of electrons in the atom is spherically symmetric, then

$$dr = 2\pi r^2 dr \sin\phi d\phi \rightarrow (2)$$

$$|\vec{s}| = 2\sin\phi$$

$$\begin{aligned} \therefore f &= \frac{2\pi}{\lambda} r S \cos\phi = \frac{4\pi}{\lambda} r \sin\phi \cos\phi \\ &= \mu r \cos\phi \rightarrow (3) \quad \text{where } \mu = \frac{4\pi}{\lambda} \sin\phi \end{aligned}$$

$$\therefore f = \int_{r=0}^{\infty} \int_{\phi=0}^{\pi} f(r) e^{i\mu r \cos\phi} 2\pi r^2 dr \sin\phi d\phi \rightarrow (4)$$

Now, $\int_0^{\pi} e^{i\mu r \cos\phi} \sin\phi d\phi$

$$= - \int_{-\pi}^{\pi} e^{i\mu r z} dz$$

$$= \int_{-1}^1 e^{i\mu r z} dz = \frac{e^{i\mu r z}}{i\mu r} \Big|_{-1}^1$$

Let, $\cos\phi = z$
 $\therefore -\sin\phi d\phi = dz$
 $\phi = 0 \rightarrow \cos\phi = 1 = z$
 $\phi = \pi \rightarrow \cos\phi = -1 = z$

$$= \frac{1}{i\mu r} [e^{i\mu r} - e^{-i\mu r}] = \left[\frac{2}{\mu r} \right] \left[\frac{e^{i\mu r} - e^{-i\mu r}}{2i} \right]$$

$$= \frac{2 \sin \mu r}{\mu r}$$

$$\therefore f = \int_0^{\infty} 4\pi r^2 f(r) \frac{\sin ur}{ur} dr \rightarrow (5)$$

(5)

The further evaluation of 'f' requires a knowledge of charge distribution in the atom. The charge distribution may be obtained from a Hartree approximation or for atoms with a large number of electrons (beyond rubidium) from a statistical model developed by Thomas and Fermi and the evaluation of 'f' may be completed.

The values of 'f' obtained by these means will be for free atoms only.

These values also represent the x-ray reflection intensities from crystal to a remarkable degree of closeness.

The Geometrical Structure Factor

The intensity of a beam diffracted by an actual ^{crystal} besides depending upon the atomic structure factors of the atoms, also depends on the contents of the unit cell, i.e., on the number, type and distribution of atoms in the unit cell. So, if we wish to discuss the characteristics of the intensity of a particular order reflection and the

(b) relative intensities of the various reflections (permitted by Bragg's law), we must take into account the contributions made by all the atoms in a unit cell to the scattered amplitude in a given direction. This is done by calculating the factor $F(h'k'l')$ for a given reflection $(h'k'l')$, and defined as the ratio of the radiation scattered by the entire unit cell to that scattered by a point electron at the origin for the same incident beam. Therefore,

$$F(h'k'l') = \sum_j f_j e^{i\phi_j} = \sum_j f_j \exp\left[\frac{2\pi i}{\lambda} (\vec{r}_j \cdot \vec{S})\right] \rightarrow (1)$$

where the sum is extended over all the atoms belonging to a unit cell, ϕ_j is the phase difference between the radiation scattered at the origin and that scattered from the j th atom of the unit cell, \vec{r}_j is the position vector of the j th atom and f_j is the atomic scattering factor of the j th atom of the unit cell. If the fractional positional coordinates of the j th atom are u_j, v_j and w_j , then

$$\vec{r}_j = u_j \vec{a} + v_j \vec{b} + w_j \vec{c}$$

$$\text{Therefore, } \vec{r}_j \cdot \vec{s} = (u_j \vec{a} + v_j \vec{b} + w_j \vec{c}) \cdot \vec{s} \quad (7)$$

$$\begin{aligned} \text{Now, } \vec{a} \cdot \vec{s} &= h' \lambda \\ \vec{b} \cdot \vec{s} &= k' \lambda \\ \vec{c} \cdot \vec{s} &= l' \lambda \end{aligned} \quad \left| \begin{array}{l} \\ \\ \end{array} \right. \quad \begin{aligned} &= (u_j h' + v_j k' + w_j l') \lambda \end{aligned}$$

$$\therefore F(h'k'l') = \sum_j f_j \exp [2\pi i (u_j h' + v_j k' + w_j l')] \quad \xrightarrow{(2)}$$

when all the atoms are identical, then all the f_j 's have the same value 'f' and eq. (2) can be written as —

$$F(h'k'l') = f S \quad \rightarrow (3)$$

$$\text{where, } S = \sum_j \exp [2\pi i (u_j h' + v_j k' + w_j l')] \quad \xrightarrow{(4)}$$

The total scattered amplitude is now equal to the product of the atomic scattering factor and the factor, S , which depends upon the geometrical arrangement of atoms in the unit cell. This factor is called the geometrical structure factor.

The intensity of the diffracted beams are —

$$\begin{aligned} |F|^2 &= F^* F = \left[\sum_j f_j \cos 2\pi (u_j h' + v_j k' + w_j l') \right]^2 \\ &\quad + \left[\sum_j f_j \sin 2\pi (u_j h' + v_j k' + w_j l') \right]^2 \end{aligned} \quad \xrightarrow{(5)}$$

(8)

The structure factor can cancel some of the reflections allowed by the space lattice, and the missing reflections help us in the determination of the structure of the unit cell.

Structure Factor of the sc structure

The effective number of atoms in a unit cell of simple cubic structure is 1. Assuming that it lies at the origin ~~for example~~ ($u = v = w = 0$), the structure factor f comes out to be unity. Therefore the diffraction amplitude becomes —

$$F(h'k'l') = f$$

Thus all the diffraction lines predicted by the Bragg's law would appear in the diffraction pattern provided the value of f is large enough to produce peaks of observable intensity.

Structure Factor of the bcc structure

The effective number of atoms in a bcc unit cell is 2; one occupies a corner position and the other occupies the centre

(9)

of the cube. If the coordinates of the corner atom is arbitrarily taken as $(0, 0, 0)$, then the coordinates of the other atom becomes $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, i.e., $u_1 = v_1 = w_1 = 0$ and $u_2 = v_2 = w_2 = \frac{1}{2}$.

$$\therefore F(h'k'l') = f \left\{ 1 + \exp [i\pi(h' + k' + l')] \right\}$$

where f is the form factor of an atom. The value of f is zero whenever the exponential has the value of -1 , which is whenever its argument is $i\pi$ times an odd integer.

$\therefore f = 0$ when $h' + k' + l' = \text{odd integer}$

$f = 2f$ when $h' + k' + l' = \text{even integer}$

Metallic sodium has a bcc structure. The diffraction spectrum does not contain lines such as (100) , (300) , (111) or (221) but lines such as (200) , (110) and (222) will be present. What are the physical interpretation of the result that the (100) reflection vanishes? The (100) reflection normally occurs when the reflections from the planes that bound the cubic cell differ in phase by 2π . In the bcc structure, there is an intervening plane of atoms (Fig. 2), labelled as second plane

10)

in the figure, which is equal in scattering power to the other planes. Situated midway between them, it gives a reflection retarded in phase by π w.r.t. the first plane, thereby cancelling the contribution from that plane. The cancellation of the (100) reflection occurs in the bcc structure because the planes are identical in composition. A similar cancellation can easily be found in hcp structure.

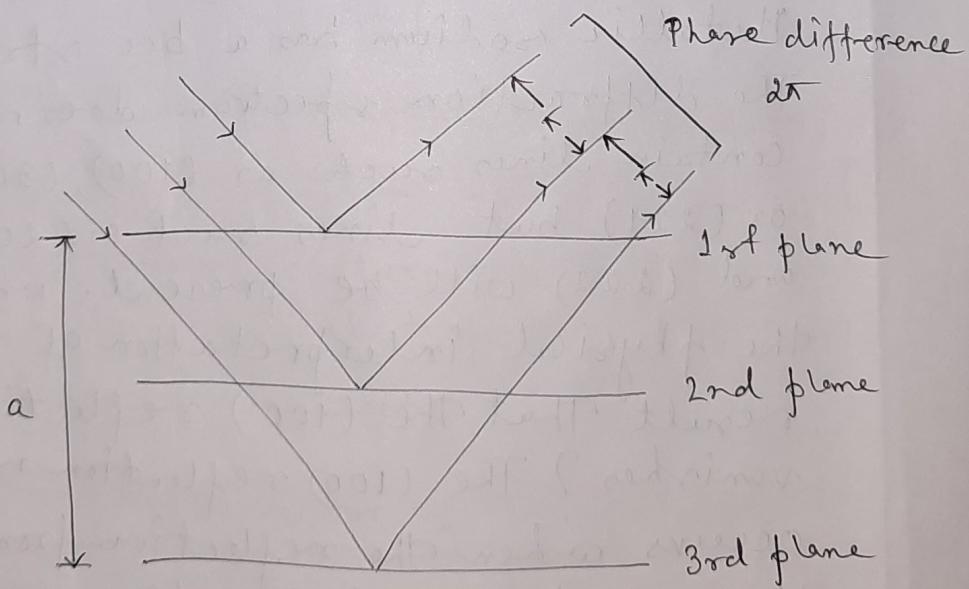


Fig. 2.

Structure factor of the fcc structure

An fcc unit cell has four identical atoms. One of these atoms is contributed by corners and may arbitrarily assigned coordinates $(0,0,0)$, whereas the other three are contributed by face centres and have the coordinates $(\frac{1}{2}, 0, \frac{1}{2})$, $(\frac{1}{2}, \frac{1}{2}, 0)$ and $(0, \frac{1}{2}, \frac{1}{2})$. Therefore,

$$F(h'k'l') = f \left\{ 1 + \exp [i\pi(h+l)] + \exp [i\pi(h+k)] + \exp [i\pi(k+l)] \right\}$$

If all the indices are even integers, $S = 4f$. Similarly, if all the indices are odd integers, $S = 4f$. But if only one of the integers is even, $S = 0$. Similarly, if only one of the integers is odd, $S = 0$. Thus, in fcc structure, no reflection can occur for which the indices are partly even or partly odd.

Both KCl and KBr have an fcc lattice. In KCl, the number of electrons in K^+ and Cl^- ions are equal. The scattering amplitudes $f(K^+)$ and $f(Cl^-)$ are almost exactly equal, so the crystal looks to x-rays as if it were a monoatomic

1d

simple cubic lattice of lattice constant $\left(\frac{a}{2}\right)$. Only even integers occur in the reflection indices.

In KBr, the form factor of Br^- is quite different than that of K^+ and all reflections of the fcc lattice are present.