1.4.2 Laue Equations

A slightly more elegant discussion of diffraction from a crystal can be obtained as follows:

(i) let $\hat{s}_0$ be a unit vector in the direction of the incident wave, and $\hat{s}$ be a unit vector in the direction of the scattered wave.
(ii) let $\mathbf{R}_1$ and $\mathbf{R}_2$ be the position vectors of a pair of atoms in a Bravais lattice, and let $\mathbf{r}_{12} = \mathbf{R}_1 - \mathbf{R}_2$.

Let us consider the waves scattered by $\mathbf{R}_1$ and by $\mathbf{R}_2$ and traveling different path lengths as shown in Figure 1.18. The difference in path length is $\mid \overline{R_2A} - \overline{BR_1} \mid$. But this is clearly equal to $|\mathbf{r}_{12} \cdot \hat{s} - \mathbf{r}_{12} \cdot \hat{s}_0|$. We define $\mathbf{S}$ as $\mathbf{S} = \hat{s} - \hat{s}_0$; then the difference in path length for the two rays is given by

$$\Delta = |\mathbf{r}_{12} \cdot \mathbf{S}|. \tag{1.11}$$

For constructive interference, this must be equal to an integral number of wave length. Thus we obtain

$$\mathbf{r}_{12} \cdot \mathbf{S} = m\lambda, \tag{1.12}$$

where m is an integer and λ is the wave length. To obtain constructive interference from every atom in the Bravais lattice, this must be true for every lattice vector $\mathbf{R}_n$. Constructive interference will occur only if

$$\mathbf{R_n} \cdot \mathbf{S} = \text{integer} \times \lambda \tag{1.13}$$

for every lattice vector $\mathbf{R_n}$ in the crystal. Of course there will be different integers for different $\mathbf{R_n}$ in general. Recall that

$$\mathbf{R_n} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3. \tag{1.14}$$

The condition Eq.(1.13) is obviously satisfied if

$$\mathbf{a}_i \cdot \mathbf{S} = ph_i\lambda, \tag{1.15}$$
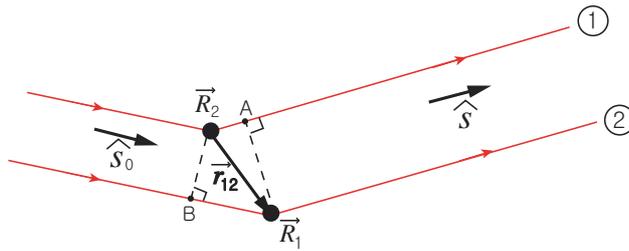
Fig. 1.18. Scattering of X-rays by a pair of atoms in a crystal

where h_i is the smallest set of integers and p is a common multiplier. We can obviously express $\mathbf{S}$ as

$$\mathbf{S} = (\mathbf{S} \cdot \mathbf{a}_1)\, \mathbf{b}_1 + (\mathbf{S} \cdot \mathbf{a}_2)\, \mathbf{b}_2 + (\mathbf{S} \cdot \mathbf{a}_3)\, \mathbf{b}_3. \tag{1.16}$$

Therefore condition Eq.(1.13) is satisfied and constructive interference from every lattice site occurs if

$$\mathbf{S} = p\,(h_1\mathbf{b}_1 + h_2\mathbf{b}_2 + h_3\mathbf{b}_3)\,\lambda, \tag{1.17}$$

or

$$\frac{\mathbf{S}}{\lambda} = p\mathbf{G_h}, \tag{1.18}$$

where $\mathbf{G_h}$ is a vector of the reciprocal lattice. Equation (1.18) is called the **Laue equation**.
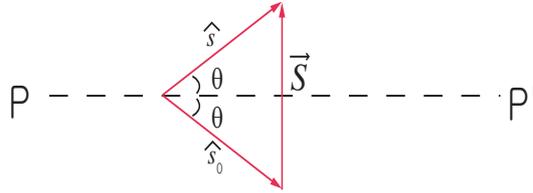
Fig. 1.19. Relation between the scattering vector $\mathbf{S} = \hat{s} - \hat{s}_0$ and the Bragg angle θ

Connection of Laue Equations and Bragg's Law

From Eq.(1.18) $\mathbf{S}$ must be perpendicular to the planes with Miller indices $(h_1 h_2 h_3)$. The distance between two planes of this set is

$$d(h_1 h_2 h_3) = \frac{2\pi}{|\mathbf{G_h}|} = p\frac{\lambda}{|\mathbf{S}|}. \tag{1.19}$$

We know that $\mathbf{S}$ is normal to the reflection plane PP' with Miller indices $(h_1 h_2 h_3)$. From Figure 1.19, it is apparent that $|\mathbf{S}| = 2\sin\theta$. Therefore, Eq.(1.19) can be written by

$$2d(h_1 h_2 h_3)\sin\theta = p\lambda,$$

where p is an integer. According to Laue's equation, associated with any reciprocal lattice vector $\mathbf{G_h} = h_1\mathbf{b}_1 + h_2\mathbf{b}_2 + h_3\mathbf{b}_3$, there is an X-ray reflection satisfying the equation $\lambda^{-1}S = pG_\mathbf{h}$, where p is an integer.

1.4.3 Ewald Construction

This is a geometric construction that illustrates how the Laue equation works. The construction goes as follows: See Figure 1.20.

1. from the origin O of the reciprocal lattice draw the vector $\overline{AO}$ of length λ^{-1} parallel to $\hat{s}_0$ and terminating on O.
2. construct a sphere of radius λ^{-1} centered at A.

If this sphere intersects a point **B** of the reciprocal lattice, then $\overline{AB} = \frac{\hat{s}}{\lambda}$ is in a direction in which a diffraction maximum occurs. Since $\overline{A_1O} = \frac{\hat{s}_0}{\lambda_1}$ and $\overline{A_1B_1} = \frac{\hat{s}}{\lambda_1}$, $\frac{\mathbf{S}}{\lambda_1} = \frac{\hat{s}-\hat{s}_0}{\lambda_1} = \overline{OB_1}$ is a reciprocal lattice vector and satisfies the Laue equation. If a higher frequency X-ray is used, λ_2, A_2, and B_2 replace λ_1, A_1, and B_1. For a continuous spectrum with $\lambda_1 \geq \lambda \geq \lambda_2$, all reciprocal lattice points between the two sphere (of radii λ_1^{-1} and λ_2^{-1}) satisfy Laue equation for some frequency in the incident beam.
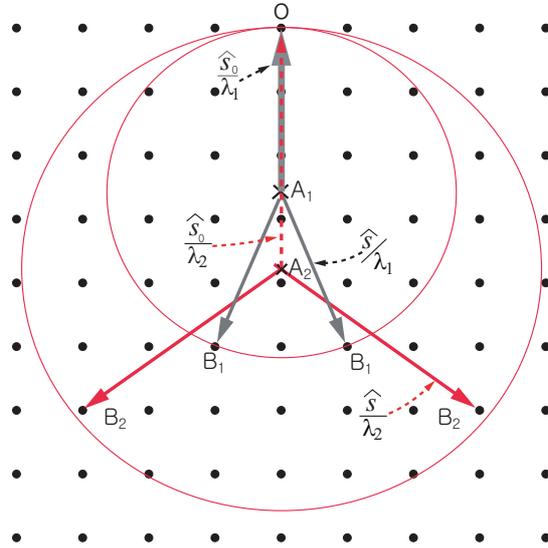
Fig. 1.20. Ewald construction for diffraction peaks

Wave vector

It is often convenient to use the set of vectors $\mathbf{K_h} = 2\pi\mathbf{G_h}$. Then, the Ewald construction gives

$$\mathbf{q}_0 + \mathbf{K_h} = \mathbf{q}, \tag{1.20}$$

where $\mathbf{q}_0 = \frac{2\pi}{\lambda}\hat{s}_0$ and $\mathbf{q} = \frac{2\pi}{\lambda}\hat{s}$ are the wave vectors of the incident and scattered waves. Equation (1.20) says that wave vector is conserved up to 2π times a vector of the reciprocal lattice.

1.4.4 Atomic Scattering Factor

It is the electrons of an atom that scatter the X-rays since the nucleus is so heavy that it hardly moves in response to the rapidly varying electric field of the X-ray. So far, we have treated all of the electrons as if they were localized at the lattice point. In fact, the electrons are distributed about the nucleus of the atom (at position $\mathbf{r} = 0$, the lattice point) with a density $\rho(\mathbf{r})$. If you know the wave function $\Psi(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_z)$ describing the z electrons of the atom, $\rho(\mathbf{r})$ is given by

$$\rho(\mathbf{r}) = \left\langle \sum_{i=1}^{z} \delta(\mathbf{r} - \mathbf{r}_i) \right\rangle = \left\langle \Psi(\mathbf{r}_1, \cdots, \mathbf{r}_z) \left| \sum_{i=1}^{z} \delta(\mathbf{r} - \mathbf{r}_i) \right| \Psi(\mathbf{r}_1, \cdots, \mathbf{r}_z) \right\rangle. \tag{1.21}$$

Now consider the difference in path length Δ between waves scattered at O and those scattered at $\mathbf{r}$.(Figure 1.21)

$$\Delta = \mathbf{r} \cdot (\hat{s} - \hat{s}_0) = \mathbf{r} \cdot \mathbf{S}. \tag{1.22}$$
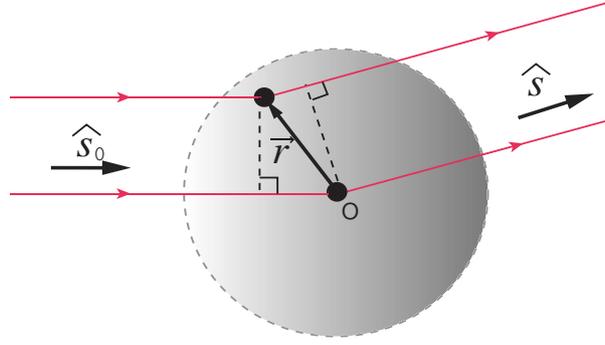
Fig. 1.21. Path difference between waves scattered at O and those at $\mathbf{r}$

The phase difference is simply $\frac{2\pi}{\lambda}$ times Δ, the difference in path length. Therefore, the scattering amplitude will be reduced from the value obtained by assuming all the electrons were localized at the origin O by a factor $z^{-1}f$, where f is given by

$$f = \int d^3r \, \rho(\mathbf{r}) \, e^{\frac{2\pi i}{\lambda} \mathbf{r} \cdot \mathbf{S}}. \tag{1.23}$$

This factor is called the **atomic scattering factor**. If $\rho(\mathbf{r})$ is spherically symmetric we have

$$f = \int_0^\infty \int_{-1}^1 2\pi r^2 dr \, d(\cos\phi)\rho(r) e^{\frac{2\pi i}{\lambda} S r \cos\phi}. \tag{1.24}$$

Recall that $S = 2\sin\theta$, where θ is the angle between $\hat{s}_0$ and the reflecting plane PP$'$ of Figure 1.19. Define μ as $\frac{4\pi}{\lambda}\sin\theta$; then f can be expressed as

$$f = \int_0^\infty dr 4\pi r^2 \rho(r)\frac{\sin\mu r}{\mu r}. \tag{1.25}$$

If λ is much larger than the atomic radius, μr is much smaller than unity wherever $\rho(r)$ is finite. In that case $\frac{\sin\mu r}{\mu r} \simeq 1$ and $f \to z$, the number of electrons.

1.4.5 Geometric Structure Factor

So far we have considered only a Bravais lattice. For a non-Bravais lattice the scattered amplitude depends on the locations and atomic scattering factors of all the atoms in the unit cell. Suppose a crystal structure contains atoms at positions $\mathbf{r}_j$ with atomic scattering factors f_j. It is not difficult to see that this changes the scattered amplitude by a factor

$$F(h_1, h_2, h_3) = \sum_j f_j e^{\frac{2\pi i}{\lambda}\mathbf{r}_j \cdot \mathbf{S}(h_1 h_2 h_3)} \tag{1.26}$$

for the scattering from a plane with Miller indices $(h_1 h_2 h_3)$. In Eq.(1.26) the position vector $\mathbf{r}_j$ of the jth atom can be expressed in terms of the primitive translation vectors $\mathbf{a}_i$

$$\mathbf{r}_j = \sum_i \mu_{ji}\mathbf{a}_i. \tag{1.27}$$

For example, in a hcp lattice $\mathbf{r}_1 = (0,0,0)$ and $\mathbf{r}_2 = (\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$ when expressed in terms of the primitive translation vectors. Of course, $\mathbf{S}(h_1 h_2 h_3)$ equal to $\lambda\sum_i h_i\mathbf{b}_i$, where $\mathbf{b}_i$ are primitive translation vectors in the reciprocal lattice. Therefore, $\frac{2\pi i}{\lambda}\mathbf{r}_j \cdot \mathbf{S}(h_1 h_2 h_3)$ is equal to $2\pi i\,(\mu_{j1}h_1 + \mu_{j2}h_2 + \mu_{j3}h_3)$, and the **structure amplitude** $F(h_1, h_2, h_3)$ can be expressed as

$$F(h_1, h_2, h_3) = \sum_j f_j e^{2\pi i\sum_i \mu_{ji}h_i}. \tag{1.28}$$

If all of the atoms in the unit cell are identical (as in diamond, Si, Ge, etc.) all of the atomic scattering factors f_j are equal, and we can write

$$F(h_1, h_2, h_3) = f\mathcal{S}(h_1 h_2 h_3). \tag{1.29}$$

The $\mathcal{S}(h_1 h_2 h_3)$ is called the **geometric structure amplitude**. It depends only on crystal structure, not on the atomic constituents, so it is the same for all hcp lattices or for all diamond lattices, *etc.*

EXAMPLE

A useful demonstration of the geometric structure factor can be obtained by considering a bcc lattice as a simple cubic lattice with two atoms in the simple cubic unit cell located at (0,0,0) and $\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$. Then

$$\mathcal{S}(h_1 h_2 h_3) = 1 + \mathrm{e}^{2\pi i \left(\frac{1}{2}h_1 + \frac{1}{2}h_2 + \frac{1}{2}h_3\right)}. \tag{1.30}$$

If $h_1 + h_2 + h_3$ is odd, $\mathrm{e}^{i\pi(h_1+h_2+h_3)} = -1$ and $\mathcal{S}(h_1 h_2 h_3)$ vanishes. If $h_1 + h_2 + h_3$ is even, $\mathcal{S}(h_1 h_2 h_3) = 2$. The reason for this effect is that the additional planes (associated with the body centered atoms) exactly cancel the scattering amplitude from the planes made up of corner atoms when $h_1 + h_2 + h_3$ is odd, but they add constructively when $h_1 + h_2 + h_3$ is even.

The scattering amplitude depends on other factors (*e.g.* thermal motion and zero point vibrations of the atoms) which we have neglected by assuming a perfect and stationary lattice.

1.4.6 Experimental Techniques

We know that constructive interference from a set of lattice planes separated by a distance d will occur when

$$2d \sin\theta = n\lambda, \tag{1.31}$$

where θ is the angle between the incident beam and the planes that are scattering, λ is the X-ray wave length, and n is an integer. For a given crystal the possible values of d are fixed by the atomic spacing, and to satisfy Eq.(1.31), one must vary either θ or λ over a range of values. Different experimental methods satisfy Eq.(1.31) in different ways. The common techniques are (i) the **Laue method**, (ii) the **rotating crystal method**, and (iii) the **powder method**.
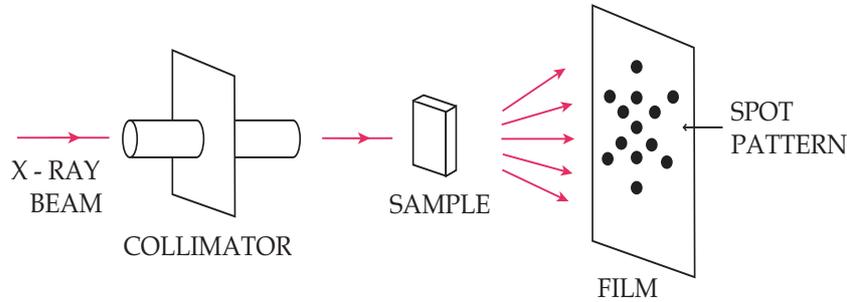
Fig. 1.22. Experimental arrangement of the Laue method

Laue Method

In this method a single crystal is held stationary in a beam of continuous wave length X-ray radiation. (Figure 1.22) Various crystal planes select the appropriate wave length for constructive interference, and a geometric arrangement of bright spots is obtained on a film.

Rotating Crystal method

In this method a monochromatic beam of X-ray is incident on a rotating single crystal sample. Diffraction maxima occur when the sample orientation relative to the incident beam satisfies Bragg's law. (Figure 1.23)
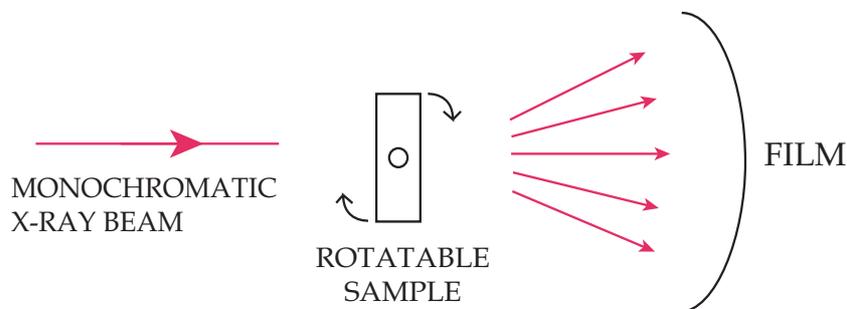
Fig. 1.23. Experimental arrangement of the rotating crystal method

Powder Method

Here a monochromatic beam is incident on a finely powdered specimen. The small crystallites are randomly oriented with respect to the incident beam, so that the reciprocal lattice structure used in the Ewald construction must be rotated about the origin of reciprocal space through all possible angles. This gives a series of spheres in reciprocal space of radii K_1, K_2, ... (we include the factor 2π in these reciprical lattice vectors) equal to the smallest, next smallest, *etc.* reciprocal lattice vectors. The sequence of values $\frac{\sin(\phi_i/2)}{\sin(\phi_1/2)}$ give the ratios of $\frac{K_i}{K_1}$ for the crystal structure. This sequence is determined by the crystal structure. Knowledge of the X-ray wave length $\lambda = \frac{2\pi}{k}$ allows determination of the lattice spacing. (Figure 1.24)
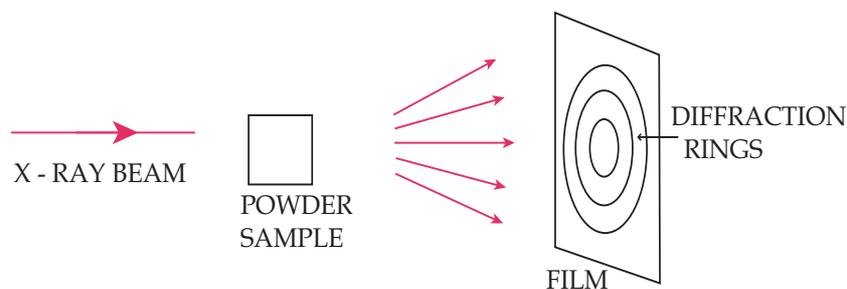
Fig. 1.24. Experimental arrangement of the powder method