



CHAPTER 2

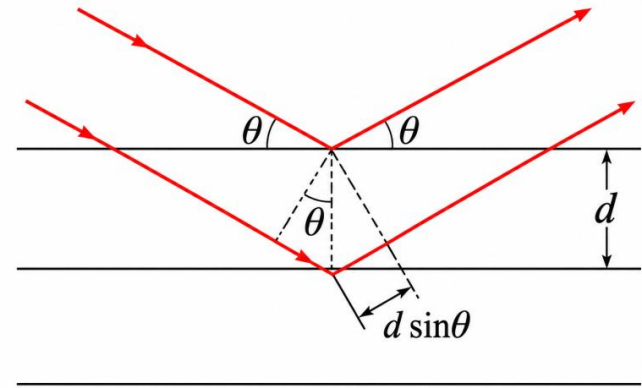
THE RECIPROCAL LATTICE

2.1 BRAGG DIFFRACTION

The crystal structure of a solid can be investigated using the diffraction of X-rays, neutrons, or electrons.

W. L. Bragg introduced a simple geometrical model to describe diffraction from crystals. Although simplified, this model correctly predicts the directions at which diffraction maxima occur.

In Bragg's model, the incident wave is regarded as being specularly reflected by parallel lattice planes. Each plane scatters only a small fraction of the incident radiation. As in specular reflection, the angle of incidence equals the angle of reflection.



A diffracted beam is observed when the waves scattered by successive parallel lattice planes interfere constructively.

Consider a set of parallel lattice planes separated by an interplanar spacing d . The path difference between waves scattered from adjacent planes is

$$2d\sin\theta$$

where θ is the angle of incidence, measured with respect to the lattice planes.

2.1 BRAGG DIFFRACTION

Constructive interference occurs when the path difference is an integer multiple of the wavelength λ :

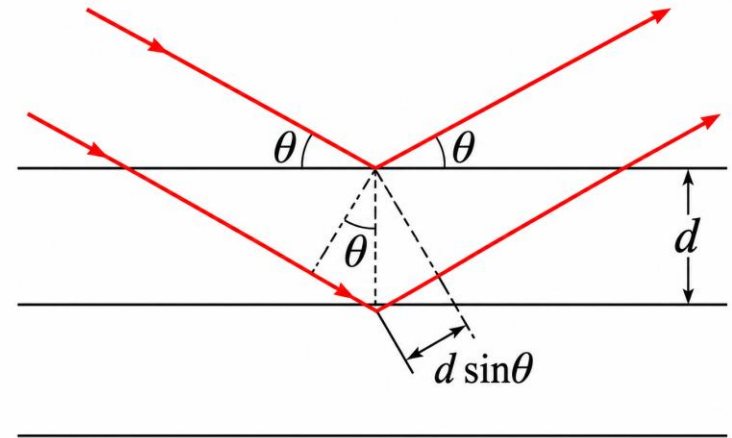
$$2d \sin \theta = n\lambda, \quad n = 1, 2, 3, \dots$$

This condition is known as **Bragg's law**.

For first-order diffraction ($n = 1$), Bragg's law can be satisfied only if

$$\lambda < 2d$$

Although the scattering from each lattice plane is specular in Bragg's geometrical model, a strong diffracted beam is observed only at angles for which the waves scattered from successive planes add in phase.



The model assumes that each lattice plane scatters only a small fraction of the incident radiation, allowing the wave to reach deeper planes. If the planes were perfect reflectors, the incident radiation would be reflected by the first plane only, and no interference between waves from successive planes could occur.

Bragg's law determines the directions of diffraction maxima from the periodicity of the lattice. It does not, by itself, determine their intensities, which also depend on the atomic basis associated with each lattice point.

2.2 RECIPROCAL LATTICE

2.2.1 Fourier analysis of the scattered wave

Bragg's derivation provides a simple condition for the occurrence of diffraction maxima, corresponding to constructive interference between waves scattered by equivalent points of the crystal lattice.

However, to calculate the intensity of a diffracted beam, it is also necessary to consider the atomic basis, namely the spatial distribution of scattering charge within the unit cell. A more detailed analysis is therefore required.

A crystal is invariant under translations of the form:

$$\vec{T} = u_1 \vec{a}_1 + u_2 \vec{a}_2 + u_3 \vec{a}_3$$

where u_1 , u_2 and u_3 are integers, and $\vec{a}_1$, $\vec{a}_2$ and $\vec{a}_3$ are the primitive translation vectors of the crystal.

Consequently, any physical quantity that shares the translational symmetry of the crystal is periodic under $\vec{T}$.

The electron density $\rho(\vec{r})$ is periodic under any lattice translation $\vec{T}$:

$$\rho(\vec{r} + \vec{T}) = \rho(\vec{r})$$

2.2 RECIPROCAL LATTICE

2.2.1 Fourier analysis of the scattered wave

For simplicity, consider a one-dimensional periodic function $\rho(x)$ with period a :

$$\rho(x + a) = \rho(x)$$

Its Fourier series expansion is

$$\rho(x) = \rho_0 + \sum_{p=1}^{\infty} \left[C_p \cos\left(\frac{2\pi p}{a} x\right) + S_p \sin\left(\frac{2\pi p}{a} x\right) \right]$$

where p is a positive integer and C_p and S_p are real Fourier coefficients.

The arguments of the sine and cosine functions ensure the periodicity of $\rho(x)$. In fact,

$$\begin{aligned} \rho(x + a) &= \rho_0 + \sum_{p=1}^{\infty} \left[C_p \cos\left(\frac{2\pi p}{a} (x + a)\right) + S_p \sin\left(\frac{2\pi p}{a} (x + a)\right) \right] \\ &= \rho_0 + \sum_{p=1}^{\infty} \left[C_p \cos\left(\frac{2\pi p}{a} x + 2\pi p\right) + S_p \sin\left(\frac{2\pi p}{a} x + 2\pi p\right) \right] \\ &= \rho(x), \quad \text{because } p \text{ is an integer and both sine and} \\ &\quad \text{cosine are periodic with period } 2\pi. \end{aligned}$$



2.2 RECIPROCAL LATTICE

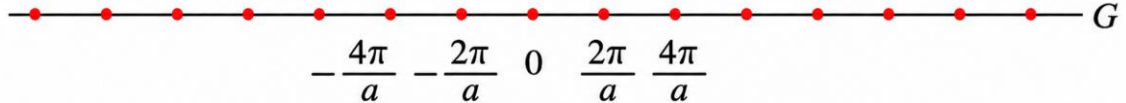
2.2.1 Fourier analysis of the scattered wave

The allowed wave vectors are

$$G_p = \frac{2\pi p}{a}, p \in \mathbb{Z}.$$

$$\rho(x) = \rho_0 + \sum_{p=1}^{\infty} \left[C_p \cos\left(\frac{2\pi p}{a}x\right) + S_p \sin\left(\frac{2\pi p}{a}x\right) \right]$$

These values define the reciprocal lattice in one dimension. The reciprocal-lattice points lie along a line, separated by the reciprocal-lattice spacing

$$\Delta G = \frac{2\pi}{a}$$


We can write the Fourier expansion in complex form as

$$\rho(x) = \sum_{p=-\infty}^{+\infty} \rho_p e^{i\frac{2\pi p}{a}x}$$

where p runs over all integers and the coefficients ρ_p are, in general, complex.

Since the electron density $\rho(x)$ must be real, the Fourier coefficients must satisfy the condition

$$\rho_{-p} = \rho_p^*$$

In particular, $\rho_0 \in \mathbb{R}$.

2.2 RECIPROCAL LATTICE

2.2.1 Fourier analysis of the scattered wave

For $p > 0$, let $\phi = \frac{2\pi p}{a}x$

and consider the pair of terms with indices p and $-p$:

$$\rho(x) = \sum_{p=-\infty}^{+\infty} \rho_p e^{i\frac{2\pi p}{a}x} \quad \rho_{-p} = \rho_p^*$$

$$\rho_p e^{i\phi} + \rho_{-p} e^{-i\phi} = (\rho_p + \rho_{-p}) \cos \phi + i(\rho_p - \rho_{-p}) \sin \phi$$

Using $\rho_{-p} = \rho_p^*$, we obtain

$$\rho_p e^{i\phi} + \rho_{-p} e^{-i\phi} = 2\operatorname{Re}(\rho_p) \cos \phi - 2\operatorname{Im}(\rho_p) \sin \phi$$

which is real. Therefore, the complete Fourier series represents a real density function.

Using the orthogonality of the complex exponential functions, the Fourier coefficients can be determined as

$$\rho_p = \frac{1}{a} \int_0^a \rho(x) e^{-i\frac{2\pi p}{a}x} dx$$

To prove this result, substitute the Fourier expansion:

$$\rho_p = \frac{1}{a} \sum_{p' \in \mathbb{Z}} \rho_{p'} \int_0^a e^{i\frac{2\pi}{a}(p'-p)x} dx$$

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2.2.1 Fourier analysis of the scattered wave

For $p' \neq p$,

$$\int_0^a e^{i\frac{2\pi}{a}(p'-p)x} dx = \frac{a}{i2\pi(p'-p)} [e^{i2\pi(p'-p)} - 1] = 0$$

$$\rho_p = \frac{1}{a} \sum_{p' \in \mathbb{Z}} \rho_{p'} \int_0^a e^{i\frac{2\pi}{a}(p'-p)x} dx$$

because $p' - p$ is a nonzero integer and therefore $e^{i2\pi(p'-p)} = 1$

For $p' = p$, $\int_0^a dx = a$.

Thus, only the term with $p' = p$ survives, giving the required coefficient ρ_p .

We now extend the Fourier analysis to a three-dimensional periodic function $\rho(\vec{r})$. By analogy with the one-dimensional case, we seek a set of vectors $\vec{G}$ such that

$$\rho(\vec{r}) = \sum_{\vec{G}} \rho_{\vec{G}} e^{i\vec{G} \cdot \vec{r}} \quad \text{with} \quad \rho_{\vec{G}} = \frac{1}{V_c} \int_{V_c} \rho(\vec{r}) e^{-i\vec{G} \cdot \vec{r}} d^3r$$

V_c volume of a primitive cell

is invariant under every lattice translation $\vec{T}$:

$$\rho(\vec{r} + \vec{T}) = \rho(\vec{r})$$

2.2 RECIPROCAL LATTICE

2.2.2 Reciprocal lattice vectors

To extend the Fourier analysis of the electron density to three dimensions, we introduce the reciprocal-lattice vectors $\vec{G}$.

The primitive vectors $\vec{b}_1$, $\vec{b}_2$, and $\vec{b}_3$ of the reciprocal lattice are defined in terms of the primitive vectors $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$ of the direct lattice as:

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

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

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

If $\vec{a}_1$, $\vec{a}_2$ and $\vec{a}_3$ are primitive vectors of the direct lattice, then $\vec{b}_1$, $\vec{b}_2$ and $\vec{b}_3$ are the corresponding primitive vectors of the reciprocal lattice.

Each reciprocal primitive vector $\vec{b}_i$ is perpendicular to the two direct-lattice primitive vectors $\vec{a}_j$ with $j \neq i$. The vectors $\vec{b}_1$, $\vec{b}_2$, and $\vec{b}_3$ satisfy:

$$\vec{b}_i \cdot \vec{a}_j = 2\pi\delta_{ij} \quad \text{where } \delta_{ij} \text{ is the Kronecker delta.}$$

2.2 RECIPROCAL LATTICE

2.2.2 Reciprocal lattice vectors

The reciprocal-lattice points are represented by the vectors:

$$\vec{G} = v_1 \vec{b}_1 + v_2 \vec{b}_2 + v_3 \vec{b}_3$$

where v_1 , v_2 , and v_3 are integers

It remains to show that, when these vectors $\vec{G}$ are used in the Fourier expansion, the resulting function is invariant under every direct-lattice translation $\vec{T} = u_1 \vec{a}_1 + u_2 \vec{a}_2 + u_3 \vec{a}_3$.

To ensure translational periodicity, we require

$$\rho(\vec{r} + \vec{T}) = \sum_{\vec{G}} \rho_{\vec{G}} e^{i\vec{G} \cdot (\vec{r} + \vec{T})} = \sum_{\vec{G}} \rho_{\vec{G}} e^{i\vec{G} \cdot \vec{r}} e^{i\vec{G} \cdot \vec{T}}.$$

$$\vec{G} \cdot \vec{T} = (v_1 \vec{b}_1 + v_2 \vec{b}_2 + v_3 \vec{b}_3) \cdot (u_1 \vec{a}_1 + u_2 \vec{a}_2 + u_3 \vec{a}_3)$$

$$\text{Since } \vec{b}_i \cdot \vec{a}_j = 2\pi \delta_{ij}$$

$$\vec{G} \cdot \vec{T} = 2\pi(v_1 u_1 + v_2 u_2 + v_3 u_3)$$

The quantity $v_1 u_1 + v_2 u_2 + v_3 u_3$ is an integer. Therefore,

$$e^{i\vec{G} \cdot \vec{T}} = e^{i2\pi(v_1 u_1 + v_2 u_2 + v_3 u_3)} = 1$$

$$\rho(\vec{r}) = \sum_{\vec{G}} \rho_{\vec{G}} e^{i\vec{G} \cdot \vec{r}}$$

$$\vec{G} = v_1 \vec{b}_1 + v_2 \vec{b}_2 + v_3 \vec{b}_3$$

$$\vec{T} = u_1 \vec{a}_1 + u_2 \vec{a}_2 + u_3 \vec{a}_3$$

2.2 RECIPROCAL LATTICE

2.2.2 Reciprocal lattice vectors

$$\rho(\vec{r}) = \sum_{\vec{G}} \rho_{\vec{G}} e^{i\vec{G} \cdot \vec{r}}$$

$$\rho(\vec{r} + \vec{T}) = \sum_{\vec{G}} \rho_{\vec{G}} e^{i\vec{G} \cdot \vec{r}} e^{i\vec{G} \cdot \vec{T}}$$

$$e^{i\vec{G} \cdot \vec{T}} = 1$$

Every Bravais lattice in direct space has an associated reciprocal lattice.

The reciprocal lattice is the set of vectors

$$\vec{G} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3, h, k, l \in \mathbb{Z},$$

which form a Bravais lattice in reciprocal space. A plane wave with wave vector $\vec{G}$ has the periodicity of the direct lattice.

As we will see, the positions of diffraction peaks map the reciprocal lattice. Their intensities also depend on the atomic basis through the structure factor.

A real-space image, when resolved at the atomic scale, provides information on the crystal structure in direct space.

The direct-lattice vectors have dimensions of length, whereas reciprocal-lattice vectors have dimensions of inverse length.

2.2 RECIPROCAL LATTICE

2.2.2 Reciprocal lattice vectors

EXERCISE 1

Consider a family of lattice planes with Miller indices (hkl) .

Show that the reciprocal lattice vector $\vec{G} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$ is perpendicular to the planes.

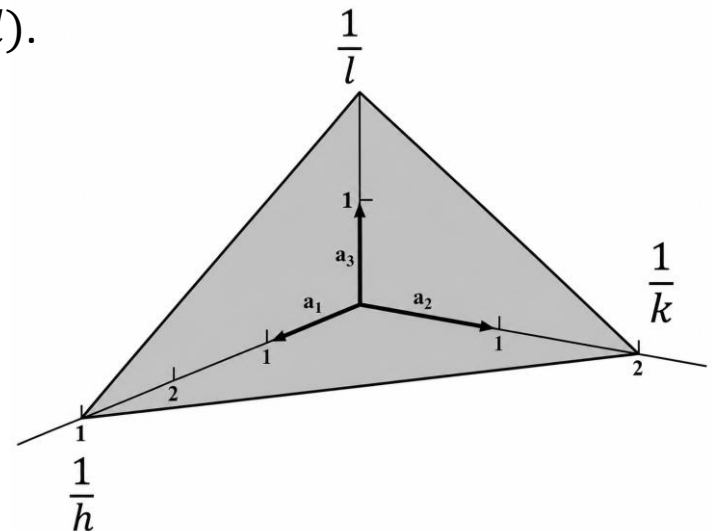
Also show that the spacing between two adjacent planes of the family is $d(hkl) = \frac{2\pi}{|\vec{G}|}$.

Let us consider a lattice plane with Miller indices (hkl) .

For h , k , and $l \neq 0$, the plane intercepts the three primitive axes at the points whose position vectors are

$$\frac{\vec{a}_1}{h}, \frac{\vec{a}_2}{k}, \frac{\vec{a}_3}{l}.$$

These three points define the plane.



2.2 RECIPROCAL LATTICE

2.2.2 Reciprocal lattice vectors

To prove that

$$\vec{G}_{hkl} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$$

is perpendicular to the plane (hkl) , it is sufficient to show that it is perpendicular to two non-parallel vectors lying in the plane.

Two such vectors are:

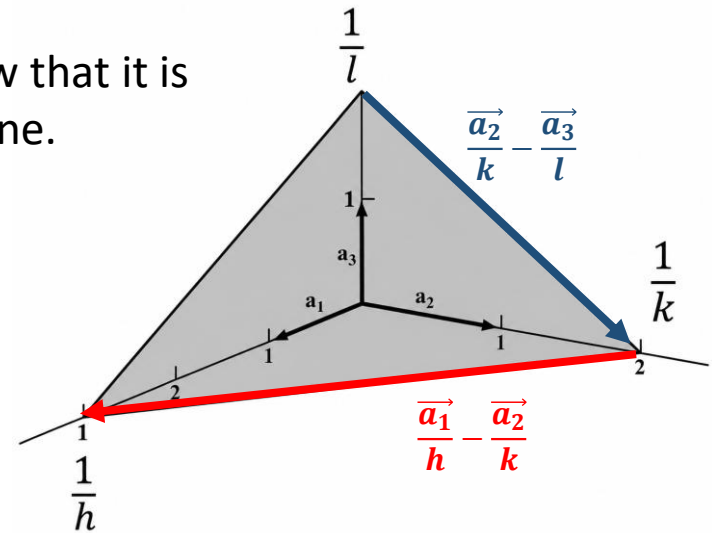
$$\vec{v}_1 = \frac{\vec{a}_1}{h} - \frac{\vec{a}_2}{k}, \quad \vec{v}_2 = \frac{\vec{a}_2}{k} - \frac{\vec{a}_3}{l}.$$

Using $\vec{b}_i \cdot \vec{a}_j = 2\pi\delta_{ij}$, we find:

$$\vec{G}_{hkl} \cdot \vec{v}_1 = (h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3) \cdot \left(\frac{\vec{a}_1}{h} - \frac{\vec{a}_2}{k} \right) = 0$$

$$\vec{G}_{hkl} \cdot \vec{v}_2 = (h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3) \cdot \left(\frac{\vec{a}_2}{k} - \frac{\vec{a}_3}{l} \right) = 0$$

Therefore, $\vec{G}_{hkl}$ is perpendicular to the plane (hkl) .



2.2 RECIPROCAL LATTICE

2.2.2 Reciprocal lattice vectors

To determine the spacing between adjacent planes of the family (hkl) , consider the plane passing through the intercept point $\frac{\vec{a}_1}{h}$.

The distance d_{hkl} from the parallel plane through the origin is the projection of this vector onto the unit normal to the planes:

$$d(hkl) = \hat{n} \cdot \frac{\vec{a}_1}{h}$$

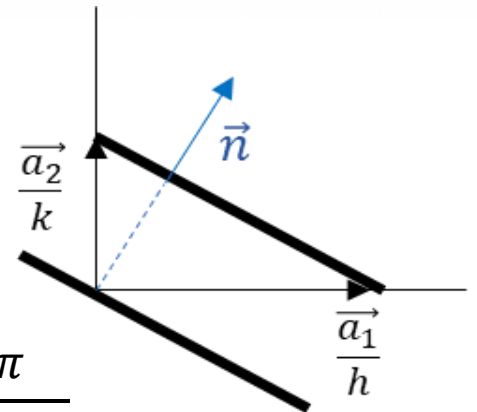
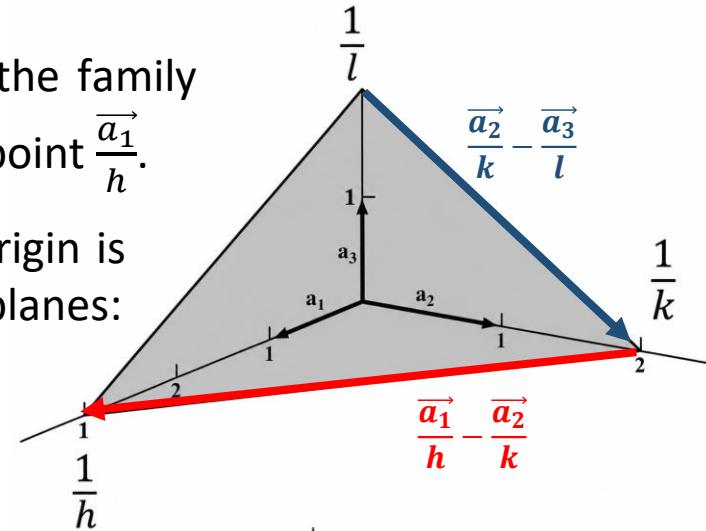
Since $\vec{G}_{hkl}$ is normal to the planes,

$$\hat{n} = \frac{\vec{G}_{hkl}}{|\vec{G}_{hkl}|}$$

Therefore,

$$d_{hkl} = \left| \frac{\vec{G}_{hkl}}{|\vec{G}_{hkl}|} \cdot \frac{\vec{a}_1}{h} \right| = \left| \frac{(h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3) \cdot \vec{a}_1}{h |\vec{G}_{hkl}|} \right| = \frac{2\pi}{|\vec{G}_{hkl}|}$$

$$\text{Thus, } d_{hkl} = \frac{2\pi}{|\vec{G}_{hkl}|}$$



2.2 RECIPROCAL LATTICE

2.2.3 Diffraction conditions

THEOREM ON THE RECIPROCAL LATTICE

The reciprocal-lattice vectors $\vec{G}$ determine the allowed momentum transfers for diffraction.

Consider a crystalline sample illuminated by an incident plane wave with wave vector $\vec{k}$. Let $\vec{k}'$ be the wave vector of the scattered wave.

At the volume element dV , located at position $\vec{r}$ with respect to the origin O , this phase shift is associated with the incident-wave phase factor

$$e^{i\vec{k}\cdot\vec{r}}$$

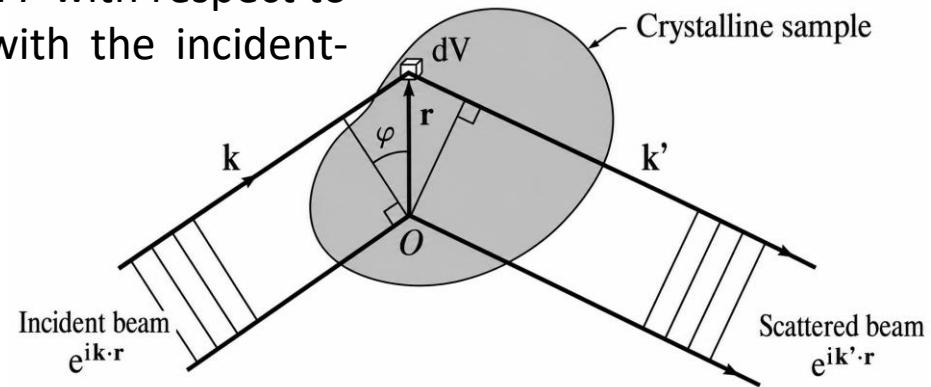
For the wave scattered in the direction $\vec{k}'$, the propagation from dV to a distant observation point introduces the relative phase factor

$$e^{-i\vec{k}'\cdot\vec{r}}$$

Therefore, the total relative phase of the wave scattered by dV is

$$e^{i(\vec{k}-\vec{k}')\cdot\vec{r}}$$

Equivalently, the phase difference is $(\vec{k} - \vec{k}') \cdot \vec{r}$



2.2 RECIPROCAL LATTICE

2.2.3 Diffraction conditions

Assume that the amplitude scattered by a volume element dV is proportional to the local electron density $\rho(\vec{r})$.

Apart from a constant prefactor, the total scattering amplitude in the direction $\vec{k}'$ is:

$$F(\Delta\vec{k}) = \int_V \rho(\vec{r}) e^{i(\vec{k}-\vec{k}')\cdot\vec{r}} dV = \int_V \rho(\vec{r}) e^{-i\Delta\vec{k}\cdot\vec{r}} dV$$

where the integral is evaluated over the crystal volume V , and

$$\Delta\vec{k} = \vec{k}' - \vec{k}$$

is the scattering vector.

Using the Fourier expansion of the electron density, we obtain:

$$\rho(\vec{r}) = \sum_{\vec{G}} \rho_{\vec{G}} e^{i\vec{G}\cdot\vec{r}}$$

$$F(\Delta\vec{k}) = \sum_{\vec{G}} \rho_{\vec{G}} \int_V e^{i(\vec{G}-\Delta\vec{k})\cdot\vec{r}} dV$$

When the scattering vector equals a reciprocal-lattice vector,

$$\Delta\vec{k} = \vec{G}$$

the contributions from all unit cells add constructively, $F = V \sum_{\vec{G}} \rho_{\vec{G}}$

2.2 RECIPROCAL LATTICE

2.2.3 Diffraction conditions

For elastic scattering, the photon energy $\hbar\omega$ is conserved. Therefore, the scattered beam has the same frequency as the incident beam and

$$|\vec{k}'| = |\vec{k}|, \quad k'^2 = k^2.$$

Starting from the diffraction condition, we can write:

$$\Delta\vec{k} = \vec{G}$$

$$\vec{k}' - \vec{k} = \vec{G}$$

or equivalently,

$$\vec{k} + \vec{G} = \vec{k}'$$

Taking the squared magnitude of both sides gives:

$$k^2 + G^2 + 2\vec{k} \cdot \vec{G} = k'^2$$

Since $k^2 = k'^2$, we have:

$$G^2 + 2\vec{k} \cdot \vec{G} = 0$$

If $\vec{G}$ is a reciprocal-lattice vector, then $-\vec{G}$ is also a reciprocal-lattice vector.

Replacing $\vec{G}$ with $-\vec{G}$, and denoting the new vector again by $\vec{G}$, gives

$$2\vec{k} \cdot \vec{G} = G^2$$

2.2 RECIPROCAL LATTICE

2.2.3 Diffraction conditions

Writing the scalar product explicitly:

$$2\vec{k} \cdot \vec{G} = G^2$$

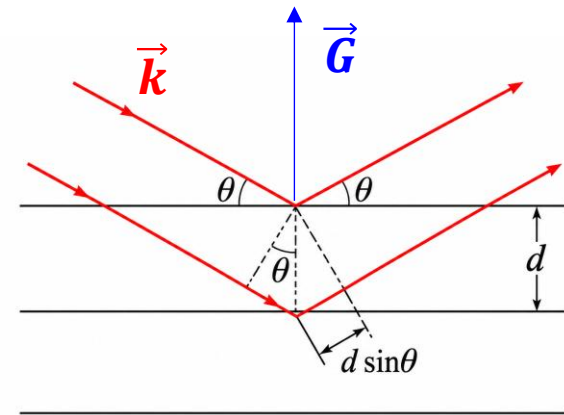
$$2|\vec{k}||\vec{G}|\cos\phi = |\vec{G}|^2 \quad \text{where } \phi \text{ is the angle between } \vec{G} \text{ and } \vec{k}.$$

From Exercise 1, the reciprocal-lattice vector $\vec{G} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$ is normal to the family of lattice planes (hkl) , whose interplanar spacing is $d(hkl) = \frac{2\pi}{|\vec{G}|}$

Since $|\vec{k}| = \frac{2\pi}{\lambda}$ and $|\vec{G}| = \frac{2\pi}{d}$, the diffraction condition becomes:

$$2\frac{2\pi}{\lambda}\cos\phi = \frac{2\pi}{d}$$

Because $\vec{G}_{hkl}$ is normal to the diffracting planes, $\phi = 90^\circ - \theta$, and therefore $\cos\phi = \sin\theta$.



Hence, $2d\sin\theta = \lambda$. This is the first-order form of Bragg's law.

More generally, if $(hkl) = n(h'k'l')$, then

$$d_{hkl} = \frac{d_{h'k'l'}}{n}$$

Thus, for the family of planes $(h'k'l')$:

$$2d_{h'k'l'}\sin\theta = n\lambda \text{ (with } n = 1, 2, 3, \dots \text{), which is Bragg's law.}$$

2.2 RECIPROCAL LATTICE

2.2.4 Laue equations

The diffraction condition $\Delta\vec{k} = \vec{G}$ can be expressed in an equivalent form known as the Laue equations.

Taking the scalar product of $\Delta\vec{k}$ with each primitive direct-lattice vector $\vec{a}_i$, we obtain.

$$\vec{a}_1 \cdot \Delta\vec{k} = 2\pi v_1$$

$$\vec{a}_2 \cdot \Delta\vec{k} = 2\pi v_2$$

$$\vec{a}_3 \cdot \Delta\vec{k} = 2\pi v_3$$

$$\vec{G} = v_1 \vec{b}_1 + v_2 \vec{b}_2 + v_3 \vec{b}_3$$

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

where v_1 , v_2 , and v_3 are integers.

These three equations are the Laue equations. Together, they are equivalent to the diffraction condition

$$\Delta\vec{k} = \vec{G}$$

For a fixed wavelength and crystal orientation, diffraction occurs only when all three equations are simultaneously satisfied. Experimentally, this condition can be met by varying the crystal orientation or the wavelength of the incident radiation.

2.2 RECIPROCAL LATTICE

2.2.4 Laue equations

The **Ewald construction** provides a geometrical representation of the diffraction condition. The points in the diagram represent reciprocal-lattice points. Choose one reciprocal-lattice point O as the endpoint of the incident wave vector $\vec{k}$.

Draw an Ewald sphere of radius

$$k = \frac{2\pi}{\lambda}$$

centred at the origin of $\vec{k}$. The sphere therefore passes through O .

A diffracted beam is produced when another reciprocal-lattice point lies on the Ewald sphere.

If this point is connected to O by the reciprocal-lattice vector $\vec{G}$, then

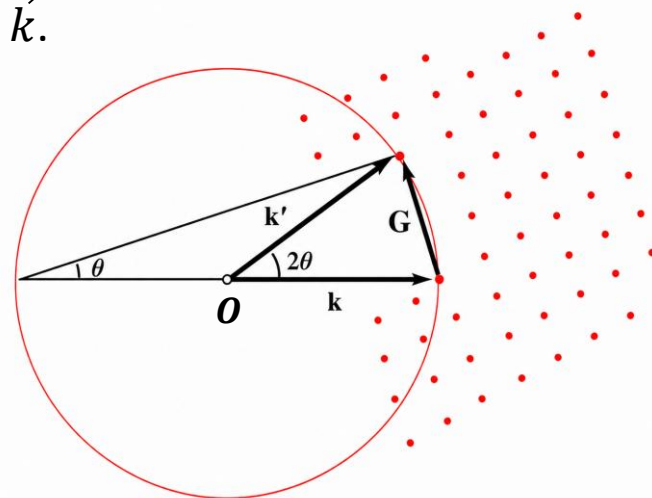
$$\vec{k}' = \vec{k} + \vec{G},$$

and hence

$$\Delta\vec{k} = \vec{k}' - \vec{k} = \vec{G}.$$

The vector $\vec{k}'$, directed from the centre of the Ewald sphere to the intersected reciprocal-lattice point, gives the direction of the diffracted beam.

If ϕ is the angle between $\vec{k}$ and $\vec{G}$, the Bragg angle is $\theta = 90^\circ - \phi$.



2.3 BRILLOUIN ZONES

Brillouin introduced a geometrical description of diffraction conditions that is fundamental to the theory of electronic energy bands in crystals.

The first Brillouin zone is the Wigner–Seitz cell of the reciprocal lattice centred at the reciprocal-lattice origin.

The Bragg condition for elastic scattering

$$2\vec{k} \cdot \vec{G} = G^2$$

also applies to electron waves in a crystal. Here, $\vec{k}$ is the electron wave vector rather than the wave vector of an incident X-ray beam.

Dividing both sides by 4, we obtain :

$$\vec{k} \cdot \left(\frac{1}{2}\vec{G}\right) = \left(\frac{1}{2}G\right)^2$$

We now work in reciprocal space, or $\vec{k}$ -space. The allowed reciprocal-lattice vectors $\vec{G}$ form a discrete lattice, whereas $\vec{k}$ is a continuous wave vector.

2.3 BRILLOUIN ZONES

Choose a reciprocal-lattice vector $\vec{G}_C$ from the origin to the reciprocal-lattice point C .

Construct the plane perpendicular to $\vec{G}_C$ at its midpoint, $\vec{G}_C/2$. This is the **Bragg plane** associated with $\vec{G}_C$ (red line 1 in the figure).

A wave vector $\vec{k}$ satisfies the Bragg condition when

$$\vec{k} \cdot \left(\frac{1}{2} \vec{G}_C \right) = \left(\frac{1}{2} \vec{G}_C \right)^2$$

Every wave vector whose endpoint lies on this plane, for example, $\vec{k}_1$, satisfies this condition:

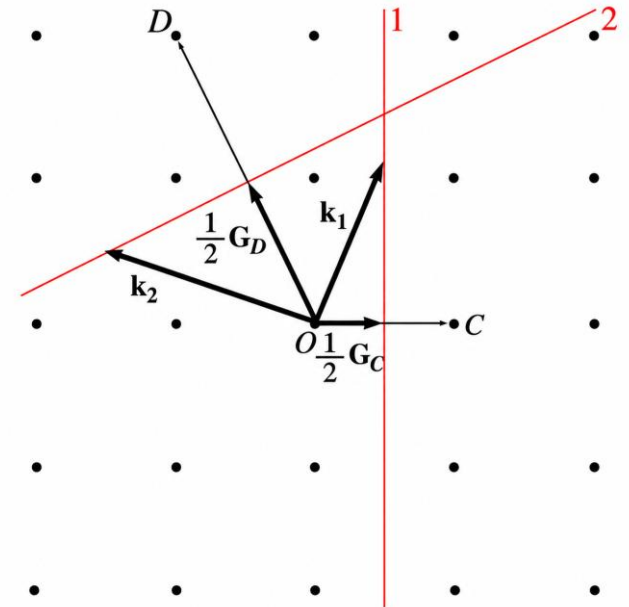
$$\vec{k}_1 \cdot \left(\frac{1}{2} \vec{G}_C \right) = \left(\frac{1}{2} \vec{G}_C \right)^2$$

In fact, writing the scalar product explicitly:

$$|\vec{k}_1| \frac{G_C}{2} \cos \theta = \left(\frac{G_C}{2} \right)^2 \quad \text{where } \theta \text{ is the angle between } \vec{k}_1 \text{ and } \vec{G}_C.$$

$$\text{Hence, } |\vec{k}_1| \cos \theta = \frac{G_C}{2}.$$

This is precisely the equation of the plane perpendicular to $\vec{G}_C$ and passing through $\vec{G}_C/2$.



2.3 BRILLOUIN ZONES

By the same reasoning, any wave vector whose endpoint lies on plane 2, such as $\vec{k}_2$, satisfies the Bragg condition associated with $\vec{G}_D$:

$$\vec{k}_2 \cdot \left(\frac{\vec{G}_D}{2} \right) = \left(\frac{G_D}{2} \right)^2$$

The planes that are perpendicular bisectors of reciprocal-lattice vectors are called **Bragg planes**.

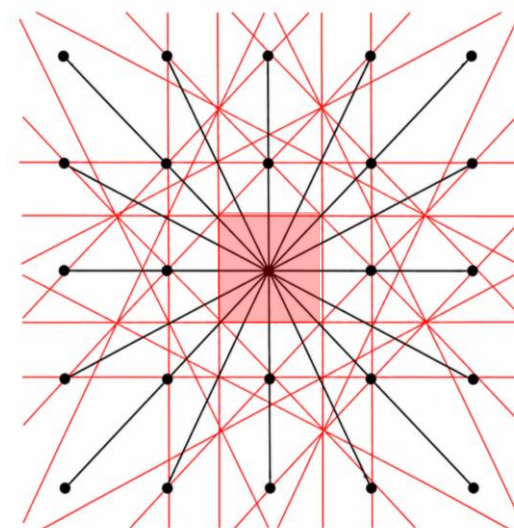
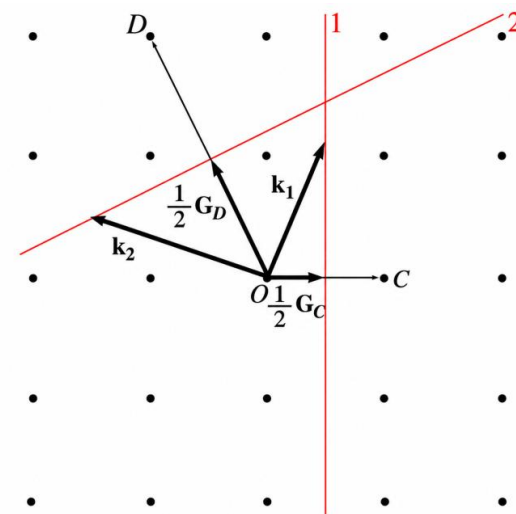
A wave vector whose endpoint lies on a Bragg plane satisfies the Bragg condition for the corresponding reciprocal-lattice vector. Together, all Bragg planes partition reciprocal space into regions called **Brillouin zones**.

In the Figure, a 2D-square reciprocal lattice is shown. The reciprocal-lattice vectors are represented by thin black lines.

The central square is the smallest region around the origin bounded entirely by these Bragg planes.

It is the Wigner–Seitz cell of the reciprocal lattice and is called the **first Brillouin zone**.

Equivalently, the first Brillouin zone is the region of $\vec{k}$ -space that can be reached from the origin without crossing any Bragg plane.



2.3 BRILLOUIN ZONES

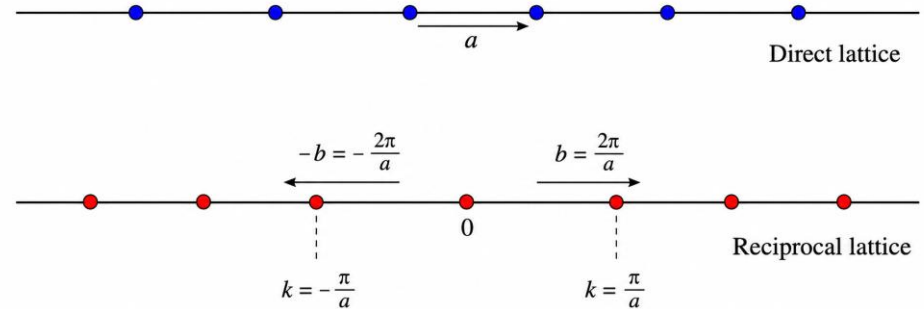
Crystal lattice and reciprocal lattice in one dimension

For a 1D direct lattice with lattice spacing a , the reciprocal-lattice primitive vector is

$$\vec{b} = \frac{2\pi}{a} \hat{x}$$

The reciprocal-lattice points are located at

$$G_n = n \frac{2\pi}{a}, n \in \mathbb{Z}.$$

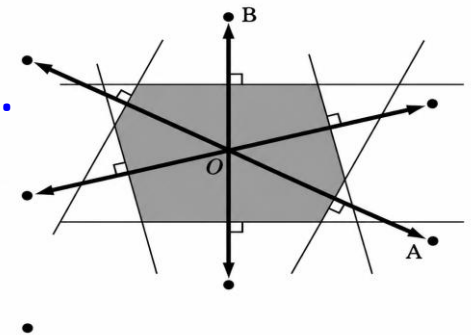


The first Brillouin zone is bounded by the points halfway between the origin and the nearest reciprocal-lattice points:

$$-\frac{\pi}{a} \leq k \leq \frac{\pi}{a}$$

Construction of the first Brillouin zone for an oblique lattice in 2D.

1. Starting from the reciprocal-lattice origin O , draw vectors to the neighbouring reciprocal-lattice points.
2. Construct the perpendicular bisector of each vector.
3. The first Brillouin zone is the region containing O that is bounded by these bisectors; equivalently, it is the Wigner–Seitz cell of the reciprocal lattice.



2.3 BRILLOUIN ZONES

2.3.1 Reciprocal lattice of a simple cubic lattice

The primitive translational vectors of a **simple cubic lattice** are:

$$\vec{a}_1 = a\hat{u}_x, \quad \vec{a}_2 = a\hat{u}_y, \quad \vec{a}_3 = a\hat{u}_z,$$

with $\hat{u}_x, \hat{u}_y, \hat{u}_z$ are mutually orthogonal unit vectors.

The primitive-cell volume is

$$V_c = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3) = a^3$$

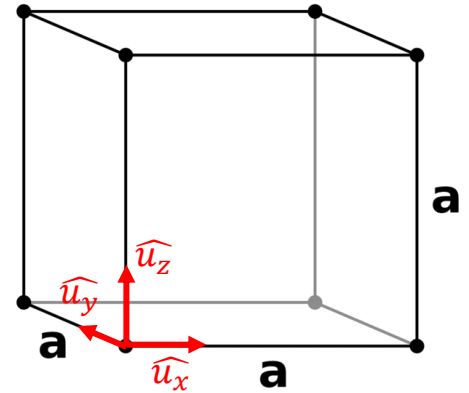
Using the general definition of the reciprocal primitive vectors,

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} = \frac{2\pi}{a} \hat{u}_x$$

$$\vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} = \frac{2\pi}{a} \hat{u}_y$$

$$\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} = \frac{2\pi}{a} \hat{u}_z$$

Therefore, the reciprocal lattice of a simple cubic lattice is also simple cubic, with lattice constant $\frac{2\pi}{a}$.



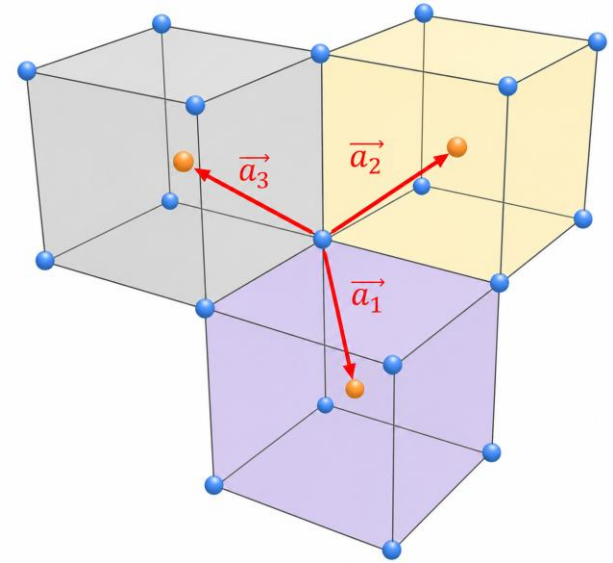
2.3 BRILLOUIN ZONES

2.3.2 Reciprocal lattice of a body-centered cubic lattice

A possible set of primitive translation vectors for the bcc lattice is:

$$\begin{aligned}\vec{a}_1 &= \frac{a}{2}(-\hat{u}_x + \hat{u}_y + \hat{u}_z) \\ \vec{a}_2 &= \frac{a}{2}(\hat{u}_x - \hat{u}_y + \hat{u}_z) \\ \vec{a}_3 &= \frac{a}{2}(\hat{u}_x + \hat{u}_y - \hat{u}_z)\end{aligned}$$

where a is the lattice constant of the conventional cubic cell and $\hat{u}_x$, $\hat{u}_y$, $\hat{u}_z$ are mutually orthogonal unit vectors parallel to its edges.



The primitive-cell volume is $V = \vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3 = \frac{1}{2} a^3$

The reciprocal primitive vectors are

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} = \frac{2\pi}{a}(\hat{u}_y + \hat{u}_z)$$

$$\vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} = \frac{2\pi}{a}(\hat{u}_x + \hat{u}_z)$$

$$\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} = \frac{2\pi}{a}(\hat{u}_x + \hat{u}_y)$$

2.3 BRILLOUIN ZONES

2.3.2 Reciprocal lattice of a body-centered cubic lattice

The reciprocal primitive vectors obtained above are precisely a set of primitive vectors for an fcc lattice. Therefore, the reciprocal lattice of a bcc lattice is fcc.

A general reciprocal-lattice vector is

$$\vec{G} = v_1 \vec{b}_1 + v_2 \vec{b}_2 + v_3 \vec{b}_3 = \frac{2\pi}{a} [(v_2 + v_3) \hat{u}_x + (v_1 + v_3) \hat{u}_y + (v_1 + v_2) \hat{u}_z]$$

where v_1 , v_2 , and v_3 are integers.

$$\vec{b}_1 = \frac{2\pi}{a} (\hat{u}_y + \hat{u}_z)$$

$$\vec{b}_2 = \frac{2\pi}{a} (\hat{u}_x + \hat{u}_z)$$

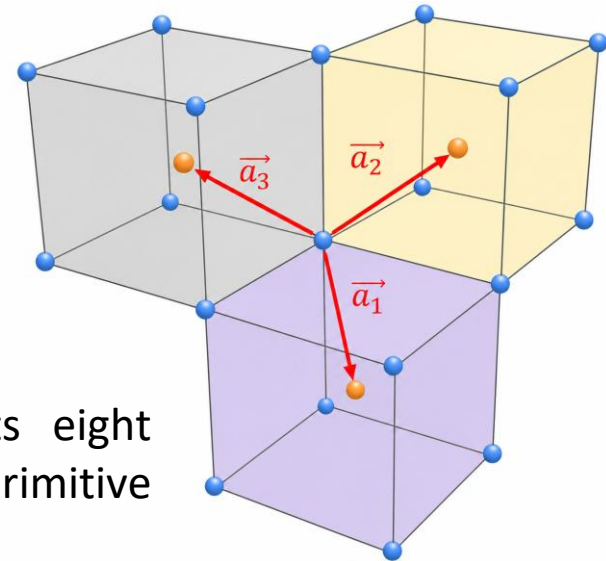
$$\vec{b}_3 = \frac{2\pi}{a} (\hat{u}_x + \hat{u}_y)$$

The volume of the reciprocal primitive cell is

$$V^* = \vec{b}_1 \cdot \vec{b}_2 \times \vec{b}_3 = 2 \left(\frac{2\pi}{a} \right)^3$$

A primitive cell of the reciprocal lattice is the parallelepiped generated by $\vec{b}_1$, $\vec{b}_2$, $\vec{b}_3$.

It contains one reciprocal-lattice point: its eight vertices are each shared by eight adjacent primitive cells, giving 1.



2.3 BRILLOUIN ZONES

2.3.2 Reciprocal lattice of a body-centered cubic lattice

The twelve shortest reciprocal-lattice vectors are

$$\frac{2\pi}{a} (\pm \hat{u}_y \pm \hat{u}_z)$$

$$\frac{2\pi}{a} (\pm \hat{u}_x \pm \hat{u}_z)$$

$$\frac{2\pi}{a} (\pm \hat{u}_x \pm \hat{u}_y)$$

$$\vec{b}_1 = \frac{2\pi}{a} (\hat{u}_y + \hat{u}_z)$$

$$\vec{b}_2 = \frac{2\pi}{a} (\hat{u}_x + \hat{u}_z)$$

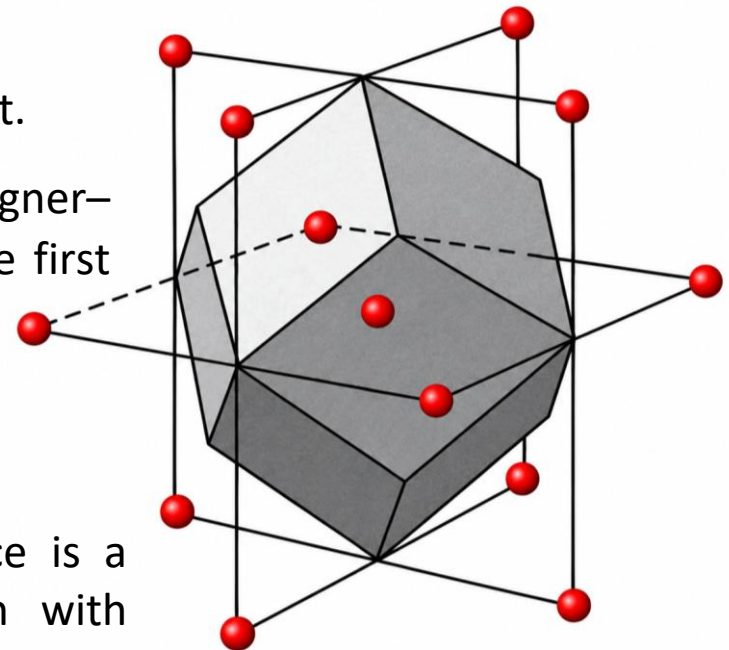
$$\vec{b}_3 = \frac{2\pi}{a} (\hat{u}_x + \hat{u}_y)$$

where the two signs in each expression are independent.

Their perpendicular-bisector planes define the Wigner-Seitz cell of the reciprocal fcc lattice, which is the first Brillouin zone of the direct bcc lattice.

The reciprocal-lattice point lies at the centre of this cell.

The first Brillouin zone of a bcc lattice is a rhombic dodecahedron, a polyhedron with twelve congruent rhombic faces.



2.3 BRILLOUIN ZONES

2.3.2 Reciprocal lattice of a face-centered cubic lattice

A possible set of primitive translation vectors for the fcc lattice is:

$$\vec{a}_1 = \frac{1}{2}a(\hat{u}_y + \hat{u}_z)$$

$$\vec{a}_2 = \frac{1}{2}a(\hat{u}_x + \hat{u}_z)$$

$$\vec{a}_3 = \frac{1}{2}a(\hat{u}_x + \hat{u}_y)$$

The primitive-cell volume is:

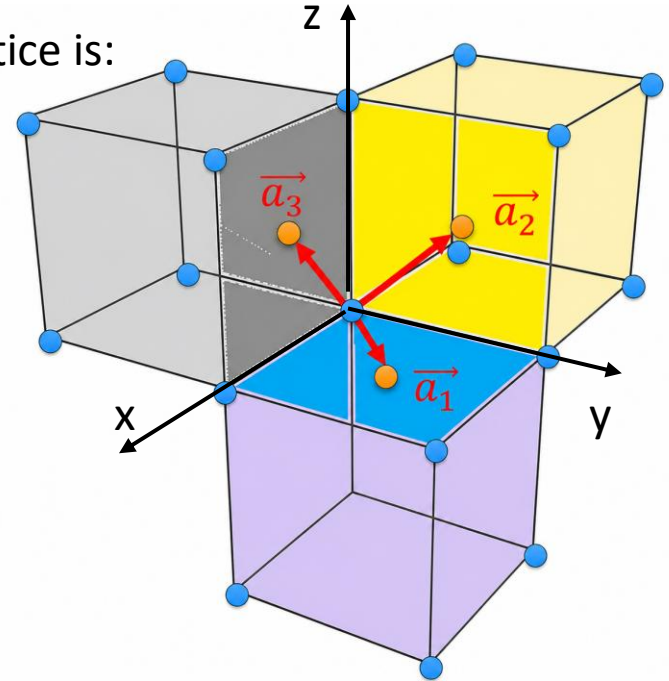
$$V = \vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3 = \frac{1}{4}a^3$$

The corresponding reciprocal primitive vectors are:

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} = \frac{2\pi}{a}(-\hat{u}_x + \hat{u}_y + \hat{u}_z)$$

$$\vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} = \frac{2\pi}{a}(\hat{u}_x - \hat{u}_y + \hat{u}_z)$$

$$\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} = \frac{2\pi}{a}(\hat{u}_x + \hat{u}_y - \hat{u}_z)$$



2.3 BRILLOUIN ZONES

2.3.2 Reciprocal lattice of a face-centered cubic lattice

The vectors $\vec{b}_1$, $\vec{b}_2$, and $\vec{b}_3$ are primitive translation vectors of a bcc lattice. Therefore, the reciprocal lattice of an fcc lattice is bcc.

The reciprocal primitive-cell volume is

$$V^* = \vec{b}_1 \cdot \vec{b}_2 \times \vec{b}_3 = 4 \left(\frac{2\pi}{a} \right)^3$$

The eight shortest reciprocal-lattice vectors are

$$\frac{2\pi}{a} (\pm \hat{u}_x \pm \hat{u}_y \pm \hat{u}_z)$$

where the three signs are independent.

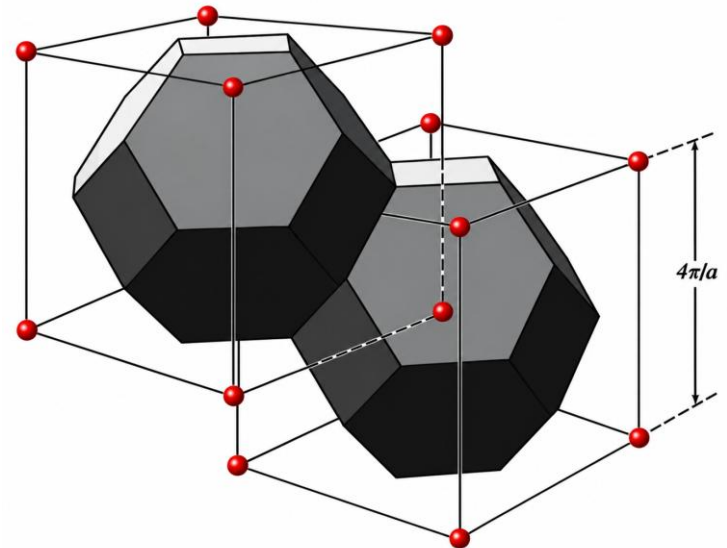
Their perpendicular-bisector planes generate the eight hexagonal faces of the first Brillouin zone.

Thus, the first Brillouin zone of an fcc lattice is a truncated octahedron, with eight hexagonal faces and six square faces.

$$\vec{b}_1 = \frac{2\pi}{a} (-\hat{u}_x + \hat{u}_y + \hat{u}_z)$$

$$\vec{b}_2 = \frac{2\pi}{a} (\hat{u}_x - \hat{u}_y + \hat{u}_z)$$

$$\vec{b}_3 = \frac{2\pi}{a} (\hat{u}_x + \hat{u}_y - \hat{u}_z)$$



2.4 FOURIER ANALYSIS OF THE BASIS

When the diffraction condition

$$\Delta \vec{k} = \vec{G}$$

is satisfied, the scattering amplitude from a crystal containing N primitive cells is

$$F_{\vec{G}} = N \int_{\text{cella}} dV n(\vec{r}) e^{-i\vec{G} \cdot \vec{r}} = N S_{\vec{G}}$$

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

with $S_{\vec{G}} = \int_{\text{cella}} dV n(\vec{r}) e^{-i\vec{G} \cdot \vec{r}}$.

is the structure factor of one primitive cell. The origin of the unit cell may be chosen at any lattice point.

Within the independent-atom approximation, the electron density in the primitive cell can be written as the sum of the atomic electron densities:

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

where s is the number of atoms in the basis, $\vec{r}_j$ is the position of atom j within the primitive cell, and $\rho_j(\vec{r} - \vec{r}_j)$ is the electron density associated with that atom.

2.4 FOURIER ANALYSIS OF THE BASIS

Inserting this last expression into $S_{\vec{G}}$ gives:

$$S_{\vec{G}} = \sum_{j=1}^s \int dV n_j(\vec{r} - \vec{r}_j) e^{-i\vec{G} \cdot \vec{r}}$$

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

For the j -th atom, introduce the local coordinate $\vec{\rho} = \vec{r} - \vec{r}_j$, $\vec{r} = \vec{\rho} + \vec{r}_j$

Then

$$e^{-i\vec{G} \cdot \vec{r}} = e^{-i\vec{G} \cdot \vec{r}_j} e^{-i\vec{G} \cdot \vec{\rho}}$$

and therefore

$$S_{\vec{G}} = \sum_{j=1}^s e^{-i\vec{G} \cdot \vec{r}_j} \int \rho_j(\vec{\rho}) e^{-i\vec{G} \cdot \vec{\rho}} d^3\rho$$

The integral defines the atomic form factor

$$f_j(\vec{G}) = \int_{\mathbb{R}^3} \rho_j(\vec{\rho}) e^{-i\vec{G} \cdot \vec{\rho}} d^3\rho$$

Hence, the structure factor can be written as

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

2.4 FOURIER ANALYSIS OF THE BASIS

The position $\vec{r}_j$ of atom j in the basis is expressed in fractional coordinates as :

$$\vec{r}_j = x_j \vec{a}_1 + y_j \vec{a}_2 + z_j \vec{a}_3$$

where x_j , y_j , and z_j are not, in general, integers.

A reciprocal-lattice vector is:

$$\vec{G} = v_1 \vec{b}_1 + v_2 \vec{b}_2 + v_3 \vec{b}_3$$

where v_1 , v_2 and v_3 are integers.

Using $\vec{b}_i \cdot \vec{a}_j = 2\pi\delta_{ij}$, we obtain

$$\vec{G} \cdot \vec{r}_j = (v_1 \vec{b}_1 + v_2 \vec{b}_2 + v_3 \vec{b}_3) \cdot (x_j \vec{a}_1 + y_j \vec{a}_2 + z_j \vec{a}_3) = 2\pi(v_1 x_j + v_2 y_j + v_3 z_j)$$

Therefore, the structure factor can be written as:

$$S_{\vec{G}} = \sum_{j=1}^s f_j e^{-i2\pi(v_1 x_j + v_2 y_j + v_3 z_j)}$$

The structure factor is generally complex. The diffracted intensity is proportional to:

$$I_{hkl} \propto |S_{hkl}|^2 = S_{hkl} S_{hkl}^*$$

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

2.4 FOURIER ANALYSIS OF THE BASIS

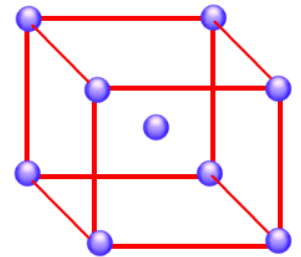
2.4.1 Structure factor of the body-centered cubic lattice

When referred to the conventional cubic cell, a bcc lattice contains two equivalent lattice points at

$$(x_1, y_1, z_1) = (0, 0, 0) \quad (x_2, y_2, z_2) = \left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$$

For identical atoms with atomic form factor f , the structure factor is:

$$S = f[1 + e^{-i\pi(v_1+v_2+v_3)}]$$



$$S_{\vec{G}} = \sum_{j=1}^s f_j e^{-i2\pi(v_1x_j+v_2y_j+v_3z_j)}$$

Therefore,

$$S = 0 \quad \text{se } v_1 + v_2 + v_3 \text{ is odd}$$

$$S = 2f \quad \text{se } v_1 + v_2 + v_3 \text{ is even}$$

Thus, bcc reflections are present only when $v_1 + v_2 + v_3$ is even.

For example, in bcc sodium the reflections (100), (300), (111), and (221) are systematically absent, whereas (200), (110), and (222) are allowed.

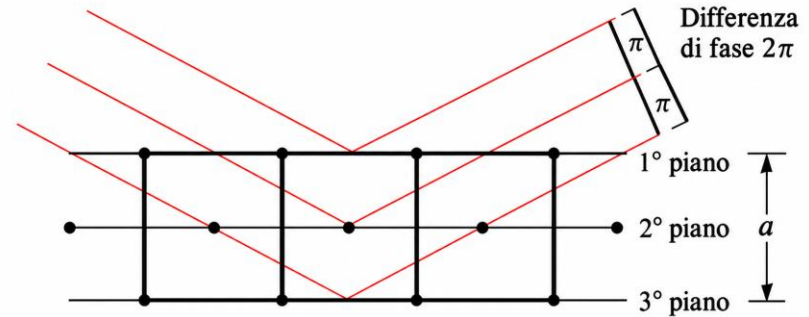
2.4 FOURIER ANALYSIS OF THE BASIS

2.4.1 Structure factor of the body-centered cubic lattice

Physical interpretation of the extinct (100) reflection?

In a simple cubic lattice, adjacent (100) planes are separated by a .

In a bcc lattice, an additional plane of equivalent atoms lies halfway between two conventional (100) planes, at a distance $a/2$.



For the (100) reflection, the scattering vector is $\vec{G}_{100} = \frac{2\pi}{a} \hat{u}_x$

The displacement from the first plane to this intermediate plane is $\Delta\vec{r} = \frac{a}{2} \hat{u}_x$

The relative phase between waves scattered by the two equivalent planes is

$$\Delta\phi = \vec{G}_{100} \cdot \Delta\vec{r} = \left(\frac{2\pi}{a} \hat{u}_x \right) \cdot \left(\frac{a}{2} \hat{u}_x \right) = \pi$$

The two scattered waves are therefore out of phase by 180° : $e^{-i\Delta\phi} = e^{-i\pi} = -1$.

Since the two planes have the same scattering amplitude f , their contributions cancel: $f + f e^{-i\pi} = f - f = 0$.

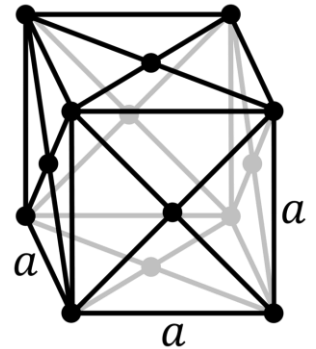
This is why the (100) reflection is systematically absent in a bcc lattice.

2.4 FOURIER ANALYSIS OF THE BASIS

2.4.2 Structure factor of the face-centered cubic lattice

When referred to the conventional cubic cell, an fcc lattice contains four equivalent lattice points at

$$(0, 0, 0), \left(0, \frac{1}{2}, \frac{1}{2}\right), \left(\frac{1}{2}, 0, \frac{1}{2}\right), \left(\frac{1}{2}, \frac{1}{2}, 0\right).$$



For identical atoms with atomic form factor f , the structure factor is:

$$S = f \left[1 + e^{-i\pi(v_2+v_3)} + e^{-i\pi(v_1+v_3)} + e^{-i\pi(v_1+v_2)} \right]$$

$$S_{\vec{G}} = \sum_{j=1}^s f_j e^{-i2\pi(v_1 x_j + v_2 y_j + v_3 z_j)}$$

If v_1 , v_2 , and v_3 are all even, each exponential is equal to +1, and $S_{v_1 v_2 v_3} = 4f$.

If v_1 , v_2 , and v_3 are all odd, each pairwise sum is even; hence, again, $S_{v_1 v_2 v_3} = 4f$.

If the indices have mixed parity—some even and some odd—the four terms cancel and:

$$S_{v_1 v_2 v_3} = 0$$

Therefore, reflections from an fcc lattice are allowed only when v_1 , v_2 , and v_3 are all even or all odd.

2.4 FOURIER ANALYSIS OF THE BASIS

2.4.3 Atomic form factor

In the expression for the structure factor, $f_j(\vec{G})$ is the atomic form factor of atom j . It is the scattering amplitude associated with the electron density of that atom.

$$S_{\vec{G}} = \sum_{j=1}^s f_j e^{-i2\pi(v_1 x_j + v_2 y_j + v_3 z_j)}$$

It has been defined as the Fourier transform of the electron density $\rho_j(\vec{r})$ associated with a single atom:

$$f_j(\vec{G}) = \int_{\mathbb{R}^3} \rho_j(\vec{r}) e^{-i\vec{G} \cdot \vec{r}} d^3 r.$$

Let θ be the angle between $\vec{G}$ and $\vec{r}$. Then:

$$\vec{G} \cdot \vec{r} = G r \cos \alpha$$

If the electron density has spherical symmetry about the atomic center, $\rho_j(\vec{r}) = \rho_j(r)$, it is convenient to use spherical coordinates with the polar axis parallel to $\vec{G}$.

Using spherical coordinates (r, α, ϑ) ,

$$\begin{cases} x = r \sin \alpha \cos \vartheta \\ y = r \sin \alpha \sin \vartheta \\ z = r \cos \alpha \end{cases} \text{ with } \begin{cases} r \in [0, +\infty) \\ \alpha \in [0, \pi] \\ \vartheta \in [0, 2\pi] \end{cases}$$

The Jacobian of the transformation is

$$J = \det \begin{pmatrix} \sin \alpha \cos \vartheta & r \cos \alpha \cos \vartheta & -r \sin \alpha \sin \vartheta \\ \sin \alpha \sin \vartheta & r \cos \alpha \sin \vartheta & r \sin \alpha \cos \vartheta \\ \cos \alpha & -r \sin \alpha & 0 \end{pmatrix} = r^2 \sin \alpha$$

2.4 FOURIER ANALYSIS OF THE BASIS

2.4.3 Atomic form factor

Therefore,

$$d^3r = dx dy dz = r^2 \sin \alpha dr d\alpha d\varphi.$$

$$f_j(\vec{G}) = \int_{\mathbb{R}^3} \rho_j(\vec{r}) e^{-i\vec{G} \cdot \vec{r}} d^3r$$

With the polar axis chosen along $\vec{G}$, the atomic form factor becomes

$$f_j(G) = \int_0^{2\pi} d\varphi \int_0^\infty r^2 dr \int_{-1}^1 \rho_j(r) e^{-iGrx} dx$$

$$\vec{G} \cdot \vec{r} = Gr \cos \alpha$$

with $x = \cos \alpha$.

Since $\rho_j(r)$ does not depend on the angular variables

$$f_j(G) = 2\pi \int_0^\infty r^2 \rho_j(r) \left[\int_{-1}^1 e^{-iGrx} dx \right] dr = 2\pi \int_0^\infty r^2 \rho_j(r) \frac{e^{iGr} - e^{-iGr}}{iGr} dr$$

Therefore

$$f_j(G) = 4\pi \int_0^\infty r^2 \rho_j(r) \frac{\sin(Gr)}{Gr} dr$$

2.4 FOURIER ANALYSIS OF THE BASIS

2.4.3 Atomic form factor

For $G = 0$, $\frac{\sin(Gr)}{Gr} \rightarrow 1$

and hence $f_j(0) = 4\pi \int_0^\infty r^2 \rho_j(r) dr = Z_j$

$$f_j(G) = 4\pi \int_0^\infty r^2 \rho_j(r) \frac{\sin(Gr)}{Gr} dr$$

where Z_j is the number of electrons of atom j .

If all the electronic charge were concentrated at $r = 0$, then $f_j(G) = Z_j$ for every G .

Thus, at zero scattering vector, the atomic form factor equals the total electronic charge of the atom, expressed in units of the electron charge.

More generally, the normalized quantity $\frac{f_j(G)}{Z_j}$

compares the scattering amplitude from the spatially extended electron cloud with that from the same number of electrons concentrated at a point.

In the independent-atom approximation, the electron density in a solid is considered as a superposition of free-atom electron densities. This approximation is accurate for the core electrons, which provide most of the X-ray scattering power. Valence electrons are redistributed when chemical bonds form. These redistributions can affect diffraction intensities.

2.5 PROBLEMS

EXERCISE 2

Show that the volume V_c^* of the primitive cell of the reciprocal lattice is $V_c^* = (2\pi)^3 / V_c$, where V_c is the volume of the primitive cell of the direct crystal.

The reciprocal primitive-cell volume is

$$V_c^* = \vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3) \quad \text{with:}$$

Let's define:

$$D = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3), \quad V_c = |D|.$$

$$V_c^* = |\vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3)| = \left| (2\pi)^3 \frac{(\vec{a}_2 \times \vec{a}_3) \cdot [(\vec{a}_3 \times \vec{a}_1) \times (\vec{a}_1 \times \vec{a}_2)]}{D^3} \right|$$

Using the vector identity $(\vec{a}_3 \times \vec{a}_1) \times (\vec{a}_1 \times \vec{a}_2) = D \vec{a}_1$

the numerator becomes $(\vec{a}_2 \times \vec{a}_3) \cdot (D \vec{a}_1) = D \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3) = D^2$

$$\text{Therefore, } V_c^* = \left| (2\pi)^3 \frac{D^2}{D^3} \right| = \frac{(2\pi)^3}{|D|} = \frac{(2\pi)^3}{V_c}$$

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

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

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

2.5 PROBLEMS

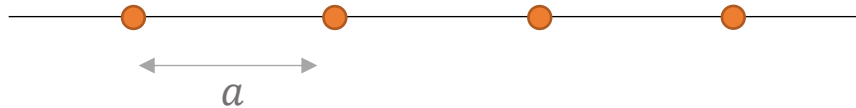
EXERCISE 3

Consider a one-dimensional chain of M identical point scatterers located at

$$\vec{r}_m = m\vec{a}, m = 0, 1, \dots, M - 1.$$

Determine the scattered intensity as a function of the scattering vector $\Delta\vec{k}$, the positions of the diffraction maxima, and their width.

Consider a linear chain with lattice spacing $a = |\vec{a}|$:



The scattering amplitude is generally: $F(\Delta\vec{k}) = \int \rho(\vec{r}) e^{-i\Delta\vec{k} \cdot \vec{r}} d^3r$

For M identical point scatterers, the electron density can be written as

$$\rho(\vec{r}) = \sum_{m=0}^{M-1} \delta(\vec{r} - \vec{r}_m)$$

Therefore, the integral becomes a sum

$$F(\Delta\vec{k}) = \sum_{m=0}^{M-1} e^{-i\Delta\vec{k} \cdot \vec{r}_m}$$

2.5 PROBLEMS

The scattering amplitude is:

$$F(\Delta\vec{k}) = \sum_{m=0}^{M-1} e^{-i\Delta\vec{k} \cdot \vec{r}_m} = \sum_{m=0}^{M-1} e^{-im\Delta\vec{k} \cdot \vec{a}}$$

Using the finite geometric-series identity

$$\sum_{m=0}^{M-1} x^m = \frac{1 - x^M}{1 - x},$$

with $x = e^{-i\Delta\vec{k} \cdot \vec{a}}$:
$$F(\Delta\vec{k}) = \frac{1 - e^{-iM\Delta\vec{k} \cdot \vec{a}}}{1 - e^{-i\Delta\vec{k} \cdot \vec{a}}}$$

The scattered intensity is proportional to the squared modulus of the amplitude:

$$I(\Delta\vec{k}) \propto |F(\Delta\vec{k})|^2 = F(\Delta\vec{k}) F^*(\Delta\vec{k})$$

$$\begin{aligned} \text{So: } I(\Delta\vec{k}) &\propto \frac{1 - e^{-iM\Delta\vec{k} \cdot \vec{a}}}{1 - e^{-i\Delta\vec{k} \cdot \vec{a}}} \frac{1 - e^{iM\Delta\vec{k} \cdot \vec{a}}}{1 - e^{i\Delta\vec{k} \cdot \vec{a}}} = \frac{2 - e^{-iM\Delta\vec{k} \cdot \vec{a}} - e^{iM\Delta\vec{k} \cdot \vec{a}}}{2 - e^{-i\Delta\vec{k} \cdot \vec{a}} - e^{i\Delta\vec{k} \cdot \vec{a}}} \\ &= \frac{2 - 2\cos(M\Delta\vec{k} \cdot \vec{a})}{2 - 2\cos(\Delta\vec{k} \cdot \vec{a})} = \frac{\sin^2\left(\frac{1}{2}M\Delta\vec{k} \cdot \vec{a}\right)}{\sin^2\left(\frac{1}{2}\Delta\vec{k} \cdot \vec{a}\right)} \end{aligned}$$

$$\sin^2\left(\frac{\alpha}{2}\right) = \frac{1 - \cos\alpha}{2}$$

2.5 PROBLEMS

The principal diffraction maxima occur when

$$\Delta\vec{k} \cdot \vec{a} = 2\pi h \quad h \in \mathbb{Z}$$

At these points, the limit of the intensity is

$$I_{\max} \propto M^2$$

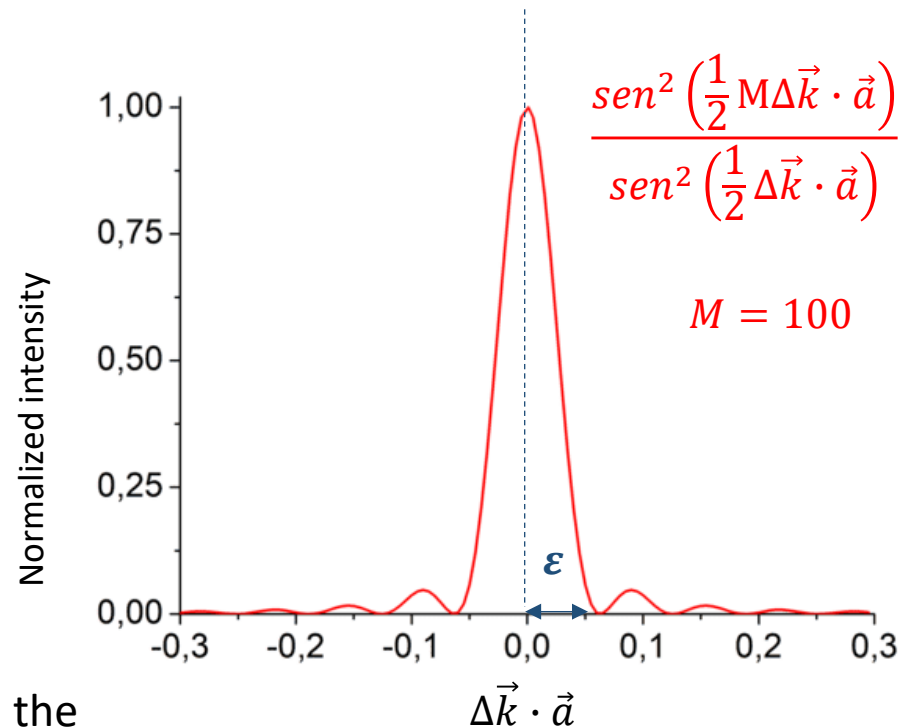
Thus, the positions of the diffraction maxima are determined by the lattice spacing a , whereas the number M of scattering centres determines their intensity and width.

To determine the width of a principal diffraction maximum, consider a small displacement ε from the maximum:

$$\Delta\vec{k} \cdot \vec{a} = 2\pi h + \varepsilon$$

where $\varepsilon = 0$ corresponds to the maximum.

$$I(\Delta\vec{k}) \propto \frac{\sin^2\left(\frac{1}{2}M\Delta\vec{k} \cdot \vec{a}\right)}{\sin^2\left(\frac{1}{2}\Delta\vec{k} \cdot \vec{a}\right)}$$



2.5 PROBLEMS

The numerator of the intensity is

$$\begin{aligned}\sin\left(\frac{M}{2}\Delta\vec{k} \cdot \vec{a}\right) &= \sin\left[M\left(\pi h + \frac{\varepsilon}{2}\right)\right] \\ &= \sin(M\pi h) \cos\left(\frac{M\varepsilon}{2}\right) + \cos(M\pi h) \sin\left(\frac{M\varepsilon}{2}\right)\end{aligned}$$

Since M and h are integers

$$\sin(M\pi h) = 0, \quad \cos(M\pi h) = \pm 1$$

Therefore,

$$\sin\left(\frac{M}{2}\Delta\vec{k} \cdot \vec{a}\right) = \pm \sin\left(\frac{M\varepsilon}{2}\right)$$

The first zeros on either side of the maximum occur when

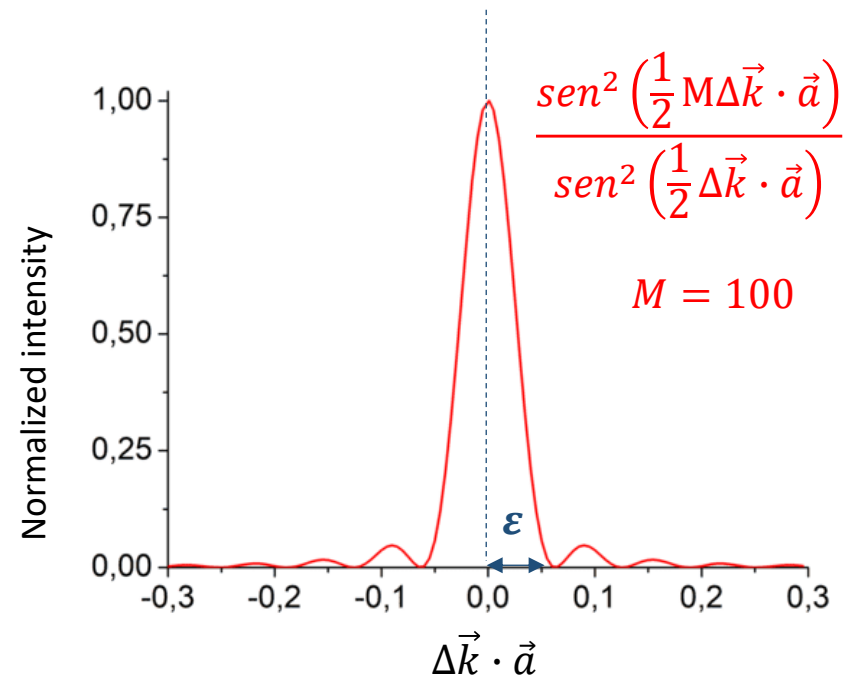
$$\frac{M\varepsilon}{2} = \pm\pi$$

that is $\varepsilon = \pm \frac{2\pi}{M}$

the full width between the first zeros is $\Delta(\Delta\vec{k} \cdot \vec{a}) = \frac{4\pi}{M}$

$$I(\Delta\vec{k}) \propto \frac{\sin^2\left(\frac{1}{2}M\Delta\vec{k} \cdot \vec{a}\right)}{\sin^2\left(\frac{1}{2}\Delta\vec{k} \cdot \vec{a}\right)}$$

$$\sin(\alpha + \beta) = \sin\alpha\cos\beta + \sin\beta\cos\alpha$$



2.5 PROBLEMS

EXERCISE 4

Determine the structure factor of the diamond structure and show that reflections are allowed when:

$h, k,$ and l are all odd,

or when

$h, k,$ and l are all even and $h + k + l = 4n, \quad n \in \mathbb{Z}.$

The diamond structure consists of two interpenetrating fcc lattices displaced by

$$\vec{d} = \frac{a}{4}(\hat{u}_x + \hat{u}_y + \hat{u}_z).$$

Its conventional cubic cell can be regarded as an fcc lattice with the two-atom basis

$$(0, 0, 0), \left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right)$$

For identical atoms with atomic form factor f , the structure factor factorises into the fcc contribution and the basis contribution:

$$S_{hkl} = S_{hkl}^{\text{basis}} \times S_{hkl}^{\text{fcc}}$$

2.5 PROBLEMS

$$S_{hkl} = S_{hkl}^{\text{basis}} \times S_{hkl}^{\text{fcc}}$$

The corresponding basis factor is

$$S_{hkl}^{\text{basis}} = f \left[1 + e^{-i\frac{1}{2}\pi(v_1+v_2+v_3)} \right]$$

$$S_{\vec{G}} = \sum_{j=1}^s f_j e^{-i2\pi(v_1x_j+v_2y_j+v_3z_j)}$$

The fcc lattice factor is

$$S_{hkl}^{\text{fcc}} = 1 + e^{-i\pi(v_2+v_3)} + e^{-i\pi(v_1+v_3)} + e^{-i\pi(v_1+v_2)}$$

Therefore, the structure factor of the diamond structure is

$$S = f \left[1 + e^{-i\frac{1}{2}\pi(v_1+v_2+v_3)} \right] \left[1 + e^{-i\pi(v_2+v_3)} + e^{-i\pi(v_1+v_3)} + e^{-i\pi(v_1+v_2)} \right]$$

For the fcc, $S_{hkl}^{\text{fcc}} \neq 0$ only when v_1, v_2 , and v_3 are all even or all odd and $S_{hkl}^{\text{fcc}} = 4$.

For diamond, the additional basis factor is $f \left[1 + e^{-i\frac{\pi}{2}(h+k+l)} \right]$

- If v_1, v_2 , and v_3 are all even: $v_1 + v_2 + v_3 = 2m$, for which $S_{v_1v_2v_3} = 8f$.
- If v_1, v_2 , and v_3 are all odd: $v_1 + v_2 + v_3 = 2n + 1, n \in \mathbb{Z}$,

$$S_{v_1v_2v_3} = 4f \left[1 + e^{-i\frac{\pi}{2}(2n+1)} \right] = 4f(1 \pm i).$$