§2 – Diffraction methods and structure determination

2.1 Lattice Planes

We can use the *Miller index* system to identify planes within a lattice.

We will consider a 2-dimensional system because it is easier to visualise, but the Miller index system is usually applied in 3 dimensions.
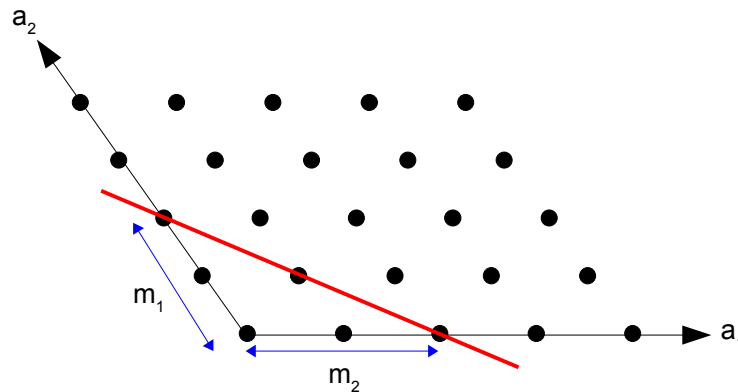

Figure 2.1: Diagram of lattice points with intersecting plane (drawn in red). The lengths m_1 and m_2 are measured in units of primitive translational vectors.

The intercepts of the plane with the lattice axes are denoted m_1, m_2, m_3.

We then take the reciprocal of these lengths.

The Miller indices are then the smallest integers with the same ratio. We usually write the Miller indices in parentheses as $(h\ k\ l)$.

Taking the example shown in Fig. (2.1):

Intercepts

$$m_1 = 2 \, ; \, m_2 = 2 \, ; \, m_3 = \infty$$

Reciprocals

$$\frac{1}{m_1} = \frac{1}{2} \, ; \, \frac{1}{m_2} = \frac{1}{2} \, ; \, \frac{1}{m_3} = 0$$

Miller Indices

Multiplying by 2 gives:

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$(h\ k\ l)=(1\ 1\ 0)$

If the plane cuts an axis on the negative side of the origin, the corresponding index is negative. This is usually denoted by an overbar.

We denote sets of symmetry-equivalent planes by braces (curly brackets) around the indices.

Example

The set of cube faces is $\{1\ 0\ 0\}=(1\ 0\ 0), (0\ 1\ 0), (0\ 0\ 1), (\bar{1}\ 0\ 0), (0\ \bar{1}\ 0), (0\ 0\ \bar{1})$.

The indices $[u\ v\ w]$ are used to denote the smallest integers that have the ratio of the components of a vector in the desired direction.

For example, the a_1 axis is the $[1\ 0\ 0]$ direction, the line $a_1=-a_2;\ a_3=0;\ a_1>0$ is the $[1\ \bar{1}\ 0]$.

2.2 Bragg's Law

In 1915, W. L. Bragg presented a simple explanation of the interference effects seen in X-ray diffraction from a crystal. It can also be used to describe electron and neutron diffraction interference patterns.

Suppose that the incident waves are reflected specularly (like a mirror) from parallel planes of atoms in the crystal, where each plane reflects just a small fraction of the radiation. Then, the angle of incidence equals the angle of reflection.

Diffracted beams are detected when the reflected beams interfere constructively.

Assume elastic scattering (no energy change after reflection).

If the lattice planes are a distance d apart, the path difference for rays reflected by adjacent planes is $2\,d\sin\theta$, where θ is the angle from the plane.

Constructive interference occurs when the path difference is an integer number of wavelengths $n\lambda$, giving the well-known Bragg law:

$$2\,d\sin\theta=n\lambda \tag{2.1}$$

Equation (2.1) shows that Bragg reflection can only occur for light at a wavelength $\lambda\leq 2d$ and since $d\simeq \overset{\circ}{A}$, this explains why we cannot use visible light to produce such effects.

This simple picture of interference can take us a long way.
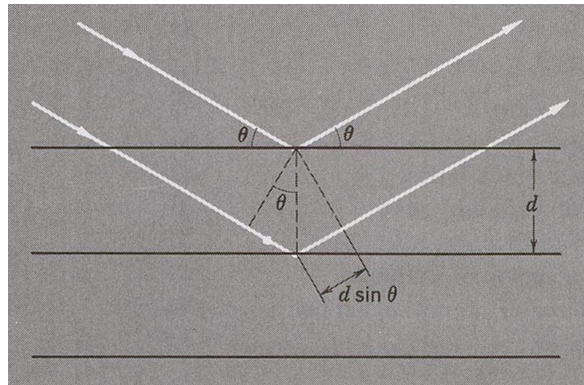
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Figure 2.2: Geometrical representation of Bragg reflection
from a plane of atoms. Here, *d* is the spacing of parallel
atomic planes. The difference in phase of waves after
reflection from successive planes is $2\pi n$.

The plane separation can be found directly from the lattice, so we can determine exactly what angles θ_{Bragg} will diffract X-rays.

Most angles do **not** correspond to a planar spacing, so there are only a few sharp peaks in the diffraction pattern.

2.3   Reciprocal Lattice Vectors

If the electron number density $n(\vec{r})$ in a crystal is a periodic function of $\vec{r}$ with periods $\vec{a}_1, \vec{a}_2, \vec{a}_3$ in the directions of the cell axes, then the number density satisfies:

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

(2.2)

Using Fourier analysis, we can show that such a periodic function in three-dimensions can be written in terms of a set of vectors $\vec{G}$:

$$n(\vec{r})=\sum_{\vec{G}} n_{\vec{G}}\exp\left(i\,\vec{G}\cdot\vec{r}\right)$$

(2.3)

These new vectors must be invariant under all $\vec{T}$ that leave the crystal invariant.

Inverting the Fourier series, integrating over the volume of a cell gives:

$$n_G=(V_{\text{cell}})^{-1}\int_{V_{\text{cell}}} dV\, n(\vec{r})\exp(i\,\vec{G}\cdot\vec{r})$$

(2.4)

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If we set $\vec{r} \rightarrow \vec{r}+\vec{T}$ into equation (2.3), we get an extra factor $\exp(i\,\vec{G}\cdot\vec{T})$.

In order to satisfy equation (2.2), we require that:

$$\vec{G}\cdot\vec{T}=2\,\pi\,(n) \tag{2.5}$$

Where: $n \in \mathbb{Z}$ (n is an integer).

Assume we can write:

$$\vec{G}=v_1\,\vec{b}_1+v_2\,\vec{b}_2+v_3\,\vec{b}_3 \tag{2.6}$$

Where v_i can be any integers.

We want to construct a set of vectors such that:

$$\vec{b}_i\cdot\vec{a}_j=2\pi\,\delta_{ij} \tag{2.7}$$

(The factor of 2π is not strictly necessary as it can be absorbed into the coefficients, and is omitted by crystallographers. However, we choose to retain it in Solid State Physics).

If $\vec{b}_i \propto \vec{a}_j \times \vec{a}_k$,where $i \neq j \neq k$, then:

$\vec{b}_i\cdot\vec{a}_j \propto a_j\cdot(\vec{a}_j \times \vec{a}_k)=0$ as required.

And:

$\vec{b}_i\cdot\vec{a}_i \propto \vec{a}_i\cdot(\vec{a}_j \times \vec{a}_k)=V_{cell}$

Thus, it is clear to see that the vectors $\vec{b}_i$ must take the form:

$$\vec{b}_1=2\,\pi\left(\frac{\vec{a}_2 \times \vec{a}_3}{V_{cell}}\right); \ \ \vec{b}_2=2\,\pi\left(\frac{\vec{a}_3 \times \vec{a}_1}{V_{cell}}\right); \ \ \vec{b}_3=2\,\pi\left(\frac{\vec{a}_1 \times \vec{a}_2}{V_{cell}}\right) \tag{2.8}$$

The vector $\vec{G}$ is called the ***reciprocal lattice vector*** and the vectors $\vec{b}_i$ are the primitive vectors of the reciprocal lattice.

Every crystal structure has a crystal lattice and a reciprocal lattice. The diffraction pattern of a crystal gives a map of the reciprocal lattice and **not** the crystal lattice.

Vectors in a reciprocal lattice have units $[L]^{-1}$, hence the term reciprocal.

A reciprocal lattice can be seen as a lattice in the Fourier space or *reciprocal space* associated with the crystal.

We can check that $\vec{b}_i$ do indeed have the correct form by checking that equation (2.3) satisfies (2.2):

$$n(\vec{r}+\vec{T})=\sum_{\vec{G}} n_{\vec{G}}\exp(i\vec{G}\cdot\vec{r})\exp(i\vec{G}\cdot\vec{T})$$

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

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

But, u_i, v_i are all integers, so all the terms in the bracket must also be an integer. Thus:

$$\exp(i\vec{G}\cdot\vec{T})=\exp[2\pi n i]=1$$

2.4 Laue Method

A travelling electromagnetic wave can be described by the wavefunction:

$$\boxed{\psi(\vec{r})=A e^{i\vec{k}\cdot\vec{r}}} \tag{2.9}$$

If A and B in Figure 2.3 are identical atoms, then the phase difference between waves scattered by each of them will be the same.

If A' is the amplitude of the scattered beam, then the scattered wave has wavefunction:

$$\boxed{\psi'(\vec{r})=A' e^{i\vec{k}'\cdot\vec{r}}} \tag{2.10}$$

We will assume elastic scattering:

$$\Rightarrow |\vec{k}|=|\vec{k}'|=\frac{2\pi}{\lambda}$$
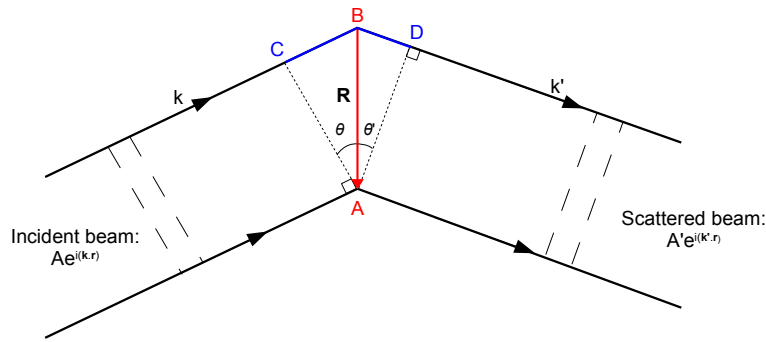
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Figure 2.3: Diagram of a wave scattering from two atoms A and B in a crystal, separated by $\vec{R}$.

From Fig. (2.3), we can see that the path difference $\overline{CB}$ of the incident wave is given by:

$$\overline{CB} = R \sin \theta$$

The phase difference is then: $\phi_{CB} = \dfrac{2\pi R}{\lambda} \sin \theta = -\vec{k} \cdot \vec{R}$.

Similarly, the phase difference of the scattered beam is: $\phi_{BD} = \dfrac{2\pi R}{\lambda} \sin \theta ' = \vec{k}' \cdot \vec{R}$

The total phase change is thus given by:

$$\phi = \phi_{BD} + \phi_{CB} = (\vec{k}' - \vec{k}) \cdot \vec{R} = \Delta \vec{k} \cdot \vec{R} \quad .$$

If the sample is a crystal, then it must be invariant to a change of $\vec{r}$ by $\vec{T}$, as shown in equation (2.2).

Thus, if the two atoms A and B are at the same position within different unit cells, we have the requirement: $\vec{R} = \vec{T}$.

For constructive interference, we require that the phase difference is an integer multiple of 2π:

$$\Delta \vec{k} \cdot \vec{T} = 2\pi n; \ \ n \in \mathbb{Z} \tag{2.11}$$

Finally, equating the right-hand sides of equations (2.5) and (2.11), we have the ***Laue condition***:

$$\Delta \vec{k} = \vec{G} \tag{2.12}$$

This condition tells us there will be diffraction (constructive interference) whenever $\Delta \vec{k}$ is equal to any one of the reciprocal lattice vectors.

This shows us that diffraction occurs only at a set of discrete points.

We note that equation (2.12) is a vector equation, so all three components must be satisfied separately. Using the orthogonality condition in equation (2.7) gives the three **Laue equations**, which must **all** be satisfied for a given $\Delta \vec{k}$. This is just a restatement of equation (2.11).

$$\vec{a}_1 \cdot \Delta \vec{k} = 2\pi v_1; \quad \vec{a}_2 \cdot \Delta \vec{k} = 2\pi v_2; \quad \vec{a}_3 \cdot \Delta \vec{k} = 2\pi v_3 \qquad (2.13)$$

2.5 Equivalence of Bragg and Laue Explanations

The points of the reciprocal lattices are normal to the planes.

In section 2.1, we defined the Miller indices $(h\,k\,l)$. These are equivalent to the integers $(v_1 v_2 v_3)$ in the reciprocal lattice vector $\vec{G}$.

The vector $\vec{G} = h\,\vec{b}_1 + k\,\vec{b}_2 + l\,\vec{b}_3$ points in a direction normal to the plane $[h\,k\,l]$.

The length of this vector is $\dfrac{2\pi}{d}$, where d is the Bragg spacing.

Since, $|\vec{k}| = |\vec{k}'|$, the vector $\Delta \vec{k}$ must point in the specular direction, as shown in Fig. 2.4 below:
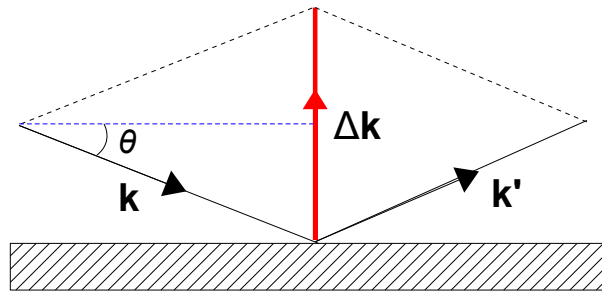

Figure 2.4: Schematic of Bragg diffraction. **Δk** is perpendicular (specular) to the Bragg plane at the scattering point.

The geometry of Fig. 2.4 shows us that:

$$\left| \Delta \vec{k} \right| = \left| \vec{G} \right| = 2 \left| \vec{k} \right| \sin\theta = \frac{2\pi}{d}$$

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Since $|\vec{k}| = \dfrac{2\pi}{\lambda}$, we have:

$2\,d\sin\theta = \lambda$, which is Bragg's law for constructive interference, where $n = 1$.

2.6 Examples of Reciprocal Lattices

a) 2D Rectangular Lattice

Let $\vec{a}_3$ point into the paper. Thus, the crystal lattice is:

$\vec{a}_2 = a_2\,\hat{y}$

$\vec{a}_1 = a_1\,\hat{x}$

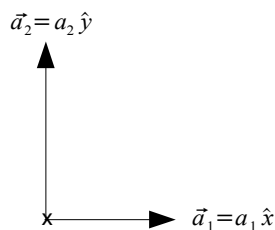**Figure 2.5**: Crystal lattice of 2-dimensional rectangular structure

From Fig. 2.5, the reciprocal lattice vectors are:

$$\vec{b}_1 = 2\pi\,\frac{a_2\,a_3}{a_1\,a_2\,a_3}\,\hat{x} = \frac{2\pi}{a_1}\,\hat{x} \quad ; \quad \vec{b}_2 = 2\pi\,\frac{a_3\,a_1}{a_1\,a_2\,a_3}\,\hat{y} = \frac{2\pi}{a_2}\,\hat{y}$$

Thus, the reciprocal lattice is:

$\vec{b}_2 = \dfrac{2\pi}{a_2}\,\hat{y}$

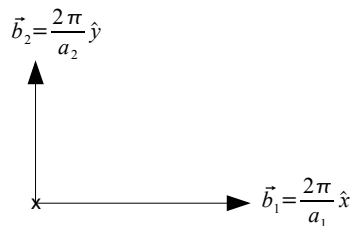$\vec{b}_1 = \dfrac{2\pi}{a_1}\,\hat{x}$

Figure 2.6: Reciprocal lattice of a 2-dimensional rectangular structure

The axis lengths in reciprocal space are in units $[L]^{-1}$ and the longer direction in real space becomes the shorter in reciprocal space and vice versa.

Note:

In the special case of the square lattice, the reciprocal lattice remains square.

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b) 2D Hexagonal Lattice

Again, let $\vec{a}_3$ point into the paper.

In this case the real lattice has the form: $a_1 = a_2 = a$; $\vec{a}_1 \cdot \vec{a}_2 = \frac{\sqrt{3}}{2} a_1 a_2 = \frac{\sqrt{3}}{2} a^2 \neq a_1 a_2$.
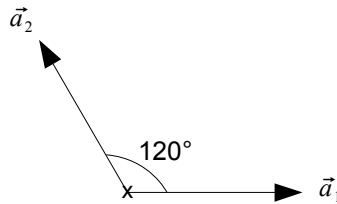

Figure 2.7: Crystal lattice of 2-dimensional hexagonal structure.

$$V_{cell} = \frac{\sqrt{3}}{2} a_1 a_2 a_3$$
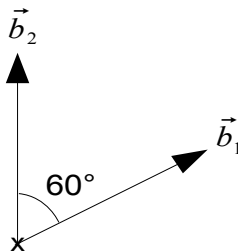
$$|b_1| = |b_2| = \frac{2}{\sqrt{3}} \frac{2\pi}{a}$$

Figure 2.8: Reciprocal lattice of a 2D hexagonal structure.

Generally, the directions of the vectors $\vec{b}_i$ are perpendicular to the vectors $\vec{a}_i$ with length proportional to $\frac{2\pi}{a_i}$.

c) FCC Lattice

The primitive lattice vectors of an fcc crystal have a more complicated relationship than either of the above examples.

We can show that the reciprocal lattice of an fcc crystal is a bcc lattice.

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Also, the reciprocal lattice of a bcc crystal is an fcc lattice.
Note:

The reciprocal of a reciprocal lattice is **always** the original lattice.

The volume of a reciprocal lattice cell is $\dfrac{(2\pi)^3}{V_{cell}}$, where: V_{cell} is the volume of the original lattice.

2.7 Diffraction from SC Lattice

a) Reciprocal View of Problem

A simple cubic lattice has a single real space lattice parameter a_0 .

The reciprocal lattice, is also a simple cubic lattice, with spacing $b_0 = \dfrac{2\pi}{a_0}$.
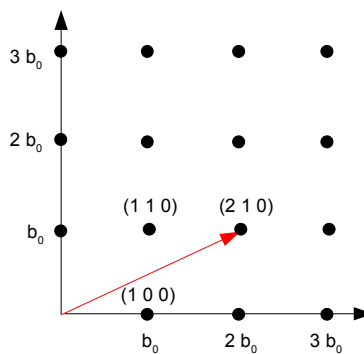

Figure 2.9: Example of a reciprocal lattice vector
in a SC crystal. Values in parentheses indicate
Miller indices.

The reciprocal lattice vector for a SC structure is given by: $\vec{G} = \dfrac{2\pi}{a_0}\left(h\,\hat{x} + k\,\hat{y} + l\,\hat{z}\right)$.

Remember, the Laue condition for diffraction is: $\Delta\vec{k} = \vec{G}$.

So, the allowed values of Δk are: $\left|\Delta\vec{k}\right| = \dfrac{2\pi}{a_0}\sqrt{h^2 + k^2 + l^2}$.

Also, $\left|\Delta\vec{k}\right| = 2k\sin\theta$, where: 2θ = Bragg angle .

A powder sample (common case) has random orientation.

Plotting intensity against Bragg angle shows a series of peaks.

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Overview of analysis procedure

1. Read off values of 2θ : the Bragg angle;

2. Convert these angles to a list of values of $|\Delta \vec{k}|^2 = \left(\dfrac{2\pi}{a_0}\right)^2 (h^2 + k^2 + l^2)$;

3. Divide by the smallest Δk^2 value to factor out a_0 ;

4. Look for simple fractions.

Note:

Not all peaks will appear. There may also be degenerate cases. This can be seen below:

(h k l)	h² + k² + l²
(1 0 0)	1
(1 1 0)	2
(1 1 1)	3
(2 0 0)	4
(2 1 0)	5
(2 1 1)	6
(2 2 0)	8
(2 2 1)	9
(3 0 0)	9

$\longrightarrow$ No peak at 7

$\left.\begin{array}{c} \\ \\ \end{array}\right\}$ degenerate

As we will see later, the peak spacings become rapidly more complicated.

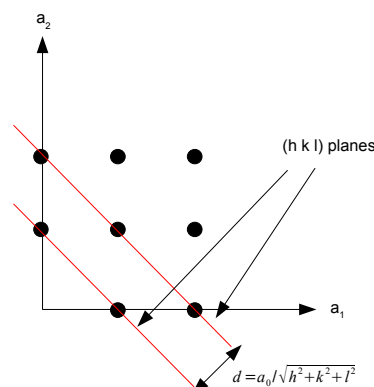Last Modified: 05/11/2006

b) Real-space View of Problem

Figure 2.10: Example of a real-space lattice in a SC crystal.

$$2\, d \sin\theta = \lambda$$

$$\Rightarrow\ d = \frac{\lambda}{2\sin\theta}$$

Analysis Procedure

1. Read off values of 2θ : the Bragg angle;

2. Convert these angles to a list of values of $\dfrac{1}{d^2} = \dfrac{1}{a_0^2}\left(h^2+k^2+l^2\right)$;

3. Divide by the smallest $\dfrac{1}{d^2}$ value to factor out a_0 ;

As can be seen, the method is the same for the real-space and reciprocal-space views: in the SC case, both are equally difficult to calculate.

The problem is that the "spacing formula" is non-trivial for more complicated lattices than the SC structure.

2.8 Lattices with a Basis

So far, we have only considered cases where $\vec{R} = \vec{T}$ when we considered diffraction.

All points that are related by lattice vectors $\vec{T}$ will be in phase whenever $\Delta\vec{k} = \vec{G}$, so they will interfere constructively.

For points in the basis, within the unit cell there will be a phase shift. Thus the interference pattern will be more complicated, **even when** $\Delta\vec{k} = \vec{G}$.

If we keep the $\Delta \vec{k} = \vec{G}$ condition, we only need to consider one unit cell.

For the general case, equation (2.11) still holds: $\Delta \vec{k} \cdot \vec{T} = 2 \pi n$.

But, we will now introduce a variable phase factor for point $\vec{r}$ in the unit cell: $\Delta \vec{k} \cdot \vec{r} \neq 2 \pi n$.

The amplitude of the interference pattern will be of the form:

$A = \sum_{\vec{r}} Weight(\vec{r}) \exp(i \vec{G} \cdot \vec{r})$. summing over points of the unit cell.

But, since the X-rays are scattered by electrons, the weight is proportional to the electron number density $n(\vec{r})$.

This Fourier series becomes an integral:

$$S_G = \int_{V_{cell}} n(\vec{r}) \exp(i \vec{G} \cdot \vec{r}) d\vec{r}$$

(2.14)

This is the ***structure factor***, and is equivalent to equation (2.4) multiplied by the volume of the unit cell.

Note:

If $\Delta \vec{k} \neq \vec{G}$, then $A(\Delta \vec{k}) = 0$.

Thus, $n(\vec{r})$ is entirely described by the (generally infinite) set of discrete complex numbers, S_G .

The important thing to note is that the measured peak intensities of Bragg diffraction are the squares of the amplitudes of the structure factors.

2.9 "Structure Factor" of an Atom

We can write the structure factor of a free atom as:

$$f_G = \int n_{atom}(\vec{r}) \exp(i \vec{G} \cdot r) d^3 \vec{r}$$

(2.15)

Crucial to this approach, most of the density of a free atom remains unchanged when it is bound in a crystal.

Thus, the functions f_G can be determined from theory.

Atoms are (to a good approximation) spherically symmetric, so are f_G . Also, to a first

approximation, we can assume that atoms are point-like.

This means that f_G are approximately converge on a single value (for a given atom) .

In fact, $f_G \simeq Z \equiv$ atomic number .

2.10 Structure Factor of a Multi-Atom Basis

Again, assume that the atoms are point-like. This means we have a set of discrete values f_j .

Thus, the structure factor integral in equation (2.15) becomes a summation:

$$S_G = \sum_j f_j \exp(i \vec{G} \cdot \vec{r}_j)$$

(2.16)

Where $\vec{r}_j \in$ unit cell is the position of the j'th atom.

The relative phases of the different points in the unit cell can often lead to cancellations, so some values of the structure factors will be zero.

We can identify different types of lattices using **selection rules**.

2.11 FCC Selection Rules

There are two ways of determining that the reciprocal lattice of an fcc crystal is a bcc:

1. Direct evaluation from the relationship between the primitive lattice vectors;
2. Evaluating as a conventional (Cartesian) unit cell and basis.

Consider the latter case.

An fcc lattice has 4 equivalent lattice points within the conventional cell, namely:

$(0\ 0\ 0), (\frac{a}{2}\ \frac{a}{2}\ 0), (\frac{a}{2}\ 0\ \frac{a}{2}), (0\ \frac{a}{2}\ \frac{a}{2})$.

These are the $\vec{r}_j$.

The reciprocal lattice of the conventional cell will also be a simple cubic:

$\vec{G} = \frac{2\pi}{a}(h, k, l)$

The structure factor is given by summing the four points:

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$$S_G = \sum_{j=1} 4\left(\exp\left(i\vec{G}\cdot r_j\right)\right) = 1 + e^{(i\pi(h+k))} + e^{(i\pi(h+l))} + e^{(i\pi(k+l))}$$

This is symmetric to permutations of h, k and l.

Thus, we have:

$$S_G = \begin{cases} 4 & (h\,k\,l) \in \{\text{¢}_{even}\} \vee \{\text{¢}_{odd}\} \\ 0 & \text{otherwise} \end{cases}$$

We can tabulate S_G against the selection rules:

Table 2.1: Structure factor and selection rules for given Miller indices for an fcc crystal.

(h k l)	S_G	$h^2+k^2+l^2$
(1 0 0)	0	1
(1 1 0)	0	2
(1 1 1)	4	3
(2 0 0)	4	4
(2 1 0)	0	5
(2 1 1)	0	6
(2 2 0)	4	8
(2 2 1)	0	9
(3 0 0)	0	9
(3 1 0)	0	10
(3 1 1)	4	11
(2 2 2)	4	12

These selection rules map exactly onto a bcc lattice, as expected.

2.12   Ewald Construction

Since $\Delta\vec{k}$ is the difference between incident and scattered wavevectors, if the scattering is elastic, we can represent it by an isosceles triangle:
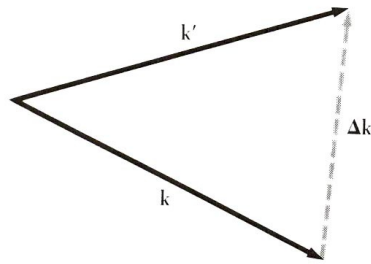
Figure 2.11: Definition of scattering vector $\Delta \vec{k}$ such that $\vec{k} + \Delta \vec{k} = \vec{k}\,'$.

Now:

1. Superimpose this isosceles triangle over the reciprocal lattice. This establishes a diffraction condition for a single crystal (generally, there is no one unique choice);

2. Fix the direction of $\vec{k}$ such that it ends on a reciprocal lattice point and draw a sphere of radius $|\vec{k}| = \dfrac{2\pi}{\lambda}$ about its origin.

3. Finally, rotate the reciprocal lattice until the sphere intersects another reciprocal lattice point.

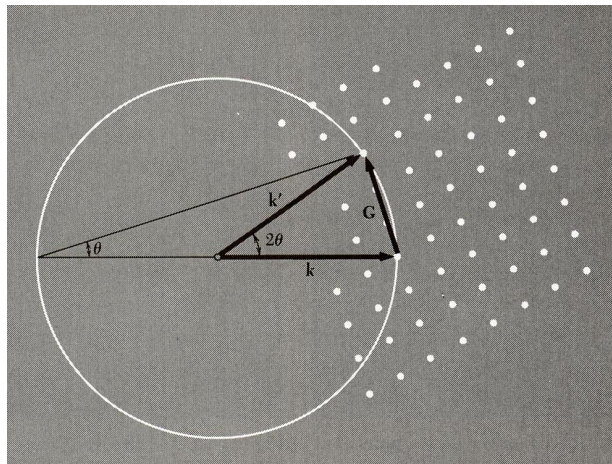Under these directives, a diffracted beam will form for an incident X-ray beam orientated along $\vec{k}$.

Figure 2.12: Diagram indicating the Ewald construction. The points on the right are reciprocal lattice points of the crystal. The vector $\vec{k}$ is drawn in the direction of the incident x-ray beam.

2.13 Zone Boundaries

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Consider a region near the origin in reciprocal space.

We want to determine the smallest value of $|\vec{k}|$ that will allow diffraction to occur independent of the direction of the vector.
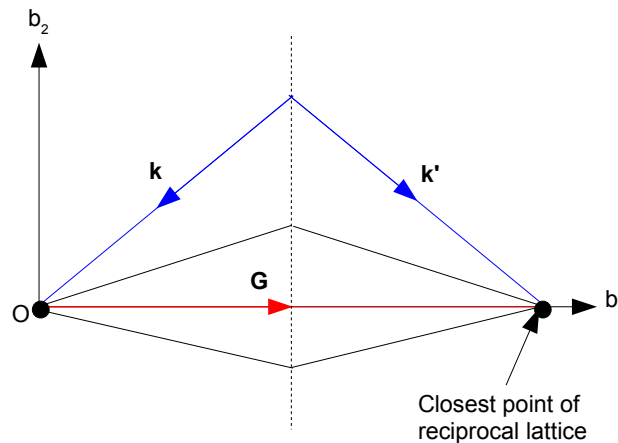

Figure 2.13: Diagram of a reciprocal lattice, with incident and diffracted wavevectors. The dashed line represent the plane for which all k-vectors represent waves that diffract.

From Fig. 2.13, we see that the minimum $|\vec{k}|$ which allows diffraction is: $k_{min} = \frac{1}{2}|\vec{G}|$.

Any waves with wavevectors of magnitude $|\vec{k}| < k_{min}$ will never experience diffraction.

2.14   Brillouin Zones

We can consider electrons within the crystal as waves, with wavevector $\vec{k}$.

For small k, the electrons are able to travel freely because they cannot undergo diffraction.

Electrons with larger values of k will be diffracted within the crystal.

The (recoprocal) space around the origin where electrons can travel freely is called the ***first Brillouin zone***.

We can see that the first Brillouin zone is simply the Wigner-Seitz primitive cell of the reciprocal lattice.
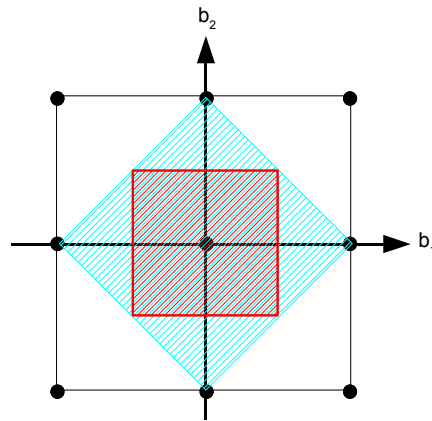
Figure 2.14: The first and second Brillouin zones for a square lattice. The 1st Brillouin zone is shown here in red, the second in cyan.

We can define higher order Brillouin zones by assembling the fragments cut off by *n*-1 bisectors where *n* is the number of the Brillouin zone.

Note:

All the Brillouin zones have the same volume $V_{rec.}$, which is the volume of the primitive cell in reciprocal space.