Identification and Determination of Crystal Structures and Orientations by Electron Diffraction

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1. Crystal and crystal lattice

A crystal is traditionally defined as a group of atoms regularly repeated indefinitely in space. The group of atoms can be represented by an equivalent point. The infinite regular array of points in space defines the crystal lattice. Let \( \mathbf{a}, \mathbf{b}, \mathbf{c} \) be three unit vectors joining nearest neighbours in three non-coplanar directions. The unit vectors define a unit cell which is a parallelepiped with 6 faces and 8 vertices. The lattice can be generated by repetition of the unit cell. When the unit vectors are mutually perpendicular, a rectangular parallelepiped with volume \( abc \) is obtained. A primitive unit cell with one lattice point is usually chosen. Sometimes, non-primitive unit cells with two (base-centred or body centred), or four lattice points (face-centred) are chosen on symmetry ground. In practice, a crystal is finite in size with a fixed number of unit cells. Macroscopically, they are specified by dimensions \( L_x \times L_y \times L_z \) along the \( \mathbf{a}, \mathbf{b}, \mathbf{c} \) axes. A unit cell of a face-centred cubic lattice (FCC) is shown is Fig. 1.1. Many metals, e.g. copper, adopt this structure. The atoms are at the corners and the face centres of the cube. The atoms touch adjacent neighbours along the face diagonals (close-packed directions). The atoms at the face centres form an octahedron. Octahedral faces are close-packed planes.

![Fig. 1.1](image)

An example of a two-dimensional crystal is an infinite sheet of stamps with each stamp as a unit cell. Since the choice of a unit cell is not unique, we can choose any equivalent point on a stamp as a lattice point, and define a vector by joining two lattice points, any cell defined by two noncollinear vectors can be chosen as a unit cell. For convenience, let us choose the corner holes of the stamps as lattice points of an infinite lattice \( L(r) \) and a stamp as a basis \( B(r) \) (Fig. 1.2). The stamp crystal \( C(r) \) can be obtained by convoluting the basis \( B(r) \) with the lattice \( L(r) \). A finite crystal with shape \( S(r) \) is obtained from the infinite crystal \( C(r) \).
\[ C(r) = B(r) \cdot L(r) \]  
\text{(crystal)}

Fig. 1.2

\[ S(r) \]  
\text{(finite crystal)}
In the determination of crystal structures by diffraction, the focus is on the size of the unit cell and the arrangement of atoms in the unit cell. But the size of crystal does have an effect on the diffraction intensity and its distribution.

1.1 Lattice points \(uvw\)

Every lattice point is defined with respect to an origin in the lattice by a vector \(\vec{r} = u\vec{a} + v\vec{b} + w\vec{c}\), where \(u, v\) and \(w\) are integers. They are written as a triple \(uvw\). The coordinates are integers for lattice points in primitive unit cells. They may be fractions when they refer to coordinates between lattice points.

The lattice points for the FCC cell are \(000\), \(\frac{1}{2}\frac{1}{2}0\), \(0\frac{1}{2}\frac{1}{2}\), \(\frac{1}{2}0\frac{1}{2}\). Why are some of the lattice points at non-integer positions?

1.2 Lattice lines \([uvw]\)

A lattice line is simply specified by the lattice vector joining two points on the line. For a lattice line passing through the origin, the lattice line is defined by the coordinates of the other point. Lattice lines are written in square brackets \([uvw]\). Lattice lines parallel to \([uvw]\) but not passing through the origin are also denoted by \([uvw]\). Thus \([uvw]\) denote a set of infinite parallel lattice lines. The angle \(\theta\) between two lattice vectors \([u_1v_1w_1]\) and \([u_2v_2w_2]\) can be determined from their dot product. For orthogonal lattices in which \(\alpha = \beta = \gamma = 90^\circ\), we have

\[
\theta = \cos^{-1}\left(\frac{u_1u_2a^2 + v_1v_2b^2 + w_1w_2c^2}{\sqrt{u_1^2a^2 + v_1^2b^2 + w_1^2c^2} \sqrt{u_2^2a^2 + v_2^2b^2 + w_2^2c^2}}\right).
\]

The cubic axes of the FCC cell are [100], [010] and [001]. Collectively, they are written \(<100>\). The face diagonals are \(<110>\). \(<110>\) are therefore close-packed directions. The body diagonals are \(<111>\).

1.3 Lattice planes \((hkl)\)

A plane in the lattice can be written

\[
\frac{X}{m} + \frac{Y}{n} + \frac{Z}{p} = 1
\]

where \(X, Y\) and \(Z\) denote the coordinates of points on the plane, and \(m, n\) and \(p\) are the intercepts of the plane on the crystallographic axes \(\vec{a}, \vec{b}, \vec{c}\) (Fig. 1.3).
The reciprocal of the intercepts, \( h = 1/m, k = 1/n \) and \( l = 1/p \), instead of the intercepts \( m, n \) and \( p \) are used to define the plane. Lattice planes, defined in terms of the smallest integral multiples of the reciprocals of the intercepts of the plane on the axes, are written as a triple \((hkl)\) in round brackets. \( h, k, l \) are known as the Miller indices.

A projection of a lattice on the \( a-b \) plane is shown in Fig. 1.4 below together with the lines representing the traces of lattice planes parallel to the \( c \) axis.

![Fig. 1.4](image)

The lattice planes are indexed as follows:

<table>
<thead>
<tr>
<th>Lattice planes</th>
<th>Intercepts</th>
<th>Reciprocal of intercepts</th>
<th>Miller indices</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2 4 ( \infty )</td>
<td>( \frac{1}{2} ) ( \frac{1}{4} ) 0</td>
<td>(210)</td>
</tr>
<tr>
<td>B</td>
<td>( \frac{1}{2} ) 3 ( \infty )</td>
<td>( \frac{1}{2} ) ( \frac{1}{3} ) 0</td>
<td>(210)</td>
</tr>
<tr>
<td>C</td>
<td>1 2 ( \infty )</td>
<td>1 ( \frac{1}{2} ) 0</td>
<td>(210)</td>
</tr>
<tr>
<td>D</td>
<td>( \frac{1}{2} ) 1 ( \infty )</td>
<td>2 1 0</td>
<td>(210)</td>
</tr>
<tr>
<td>E</td>
<td>- - -</td>
<td>- - -</td>
<td>-</td>
</tr>
<tr>
<td>F</td>
<td>( \frac{1}{2} ) ( \bar{1} ) ( \infty )</td>
<td>( \bar{2} ) ( \bar{1} ) 0</td>
<td>(( \bar{2} \bar{1}0 ))</td>
</tr>
<tr>
<td>G</td>
<td>( \bar{1} ) ( \bar{2} ) ( \infty )</td>
<td>( \bar{1} ) ( \frac{1}{2} ) 0</td>
<td>(( \bar{2} \bar{1}0 ))</td>
</tr>
</tbody>
</table>

The lattice planes A to G form a set of parallel and equally spaced planes with the same Miller indices. In general, \((hkl)\) represents an infinite set of parallel planes with spacing \( d_{hkl} \). The plane \( E \) passing through the origin cannot be indexed. \((120)\) and \((\bar{1}20)\) denote the same set of parallel planes. The equation of a set of planes can be written

\[
hX + kY + lZ = C
\]

For a given set of Miller indices \( h, k \) and \( l \), \( C = 1 \) corresponds to the plane nearest to the origin in the positive directions of \( \mathbf{a}, \mathbf{b}, \mathbf{c} \). \( C = -1 \) corresponds to the nearest plane in the negative directions of \( \mathbf{a}, \mathbf{b}, \mathbf{c} \). The plane \((hkl)\) passes through the origin is

\[
hX + kY + lZ = 0, \text{ corresponding to } C = 0.
\]

For a lattice point on the plane through the origin, its coordinates are \( uvw \), hence the equation of a lattice line \([uvw]\) on the lattice plane \((hkl)\) is
The Miller indices of the cube faces of the FCC cell are (100), (\overline{1}00), (010), (0\overline{1}0), (001) and (00\overline{1}). This set of planes are written \{100\}. The Miller indices of the planes that cut across the face diagonals on opposite sides of the cube faces are \{101\}. The Miller indices of the close-packed planes which intersect the cubic planes along <101> are \{111\}. The \{001\}, \{101\} and \{111\} planes which are the most important low index planes of the FCC lattice are shown in Fig. 1.5 together with their respective two dimensional unit cells.

![Fig. 1.5](image)

The basis vectors for the unit cell in the (001) plane are given by \( \vec{a}_1 = \frac{\sqrt{2}}{2}[110] \), \( \vec{a}_2 = \frac{\sqrt{2}}{2}[\overline{1}0] \). The basis vectors for the (101) unit cell are given by \( \vec{a}_1 = \frac{\sqrt{2}}{2}[10\overline{1}] \), \( \vec{a}_2 = \frac{\sqrt{2}}{2}[010] \). The basis vectors for the (111) unit cell are \( \vec{a}_1 = \frac{\sqrt{2}}{2}[10\overline{1}] \), \( \vec{a}_2 = \frac{\sqrt{2}}{2}[01\overline{1}] \). Notice that the basis vectors are mostly along close-packed directions.

The (001) cell is 4-fold symmetric, its point group symmetry is 4\( m\). The (101) cell is 2-fold symmetric with point group 2\( m\). The (111) cell is 6-fold symmetric with point group 6\( m\). The \{001\} planes are the cubic faces whereas the \{111\} planes are the octahedral faces.

- Identify the lattice planes in each of the two-dimensional unit cells of the (001), (101) and (111) planes in Fig. 1.5. Comment also on the stacking of the (001), (101) and (111) planes.

### 1.4 Zone and zone axis

A crystal face lies parallel to a set of lattice planes. Parallel crystal faces correspond to the same set of lattice planes. A crystal edge which is the intersection of two crystal planes is parallel to a set of lattice lines. A
set of crystal planes intersecting in parallel edges is termed a zone. The
common direction of the edges is called the zone axis. The zone axis [uvw]
of two intersecting lattice planes \((h_1k_1l_1)\) and \((h_2k_2l_2)\) can be obtained from
the zonal equation above.

\[
\begin{align*}
u : v : w &= \begin{vmatrix} k_1 & l_1 & h_1 \\ k_2 & l_2 & h_2 \end{vmatrix} \\
&= \begin{vmatrix} h_1 & k_1 \\ h_2 & k_2 \end{vmatrix} \\
&= \begin{vmatrix} k_1 & l_1 \\ k_2 & l_2 \end{vmatrix} \\
&= \begin{vmatrix} l_1 & h_1 \\ l_2 & h_2 \end{vmatrix} \\
&= \begin{vmatrix} h_1 & k_1 \\ h_2 & k_2 \end{vmatrix}
\end{align*}
\]

Equivalently, \( [uvw] \) is given by the cross product of \([h_1k_1l_1]\) and \([h_2k_2l_2]\), i.e.

\[
[uvw] = [h_1k_1l_1] \times [h_2k_2l_2].
\]

Two lattice vectors \([u_1v_1w_1]\) and \([u_2v_2w_2]\) define a lattice plane \((hkl)\),
the Miller indices of which can also be obtained from the zonal equation.

\[
\begin{align*}
h : k : l &= \begin{vmatrix} v_1 & w_1 \\ v_2 & w_2 \end{vmatrix} \\
&= \begin{vmatrix} u_1 & v_1 \\ u_2 & v_2 \end{vmatrix} \\
&= \begin{vmatrix} w_1 & v_1 \\ w_2 & v_2 \end{vmatrix}
\end{align*}
\]

Equivalently, the normal of the plane \((hkl)\), \(\vec{g}_{hkl}\), is given by the cross
product of \([u_1v_1w_1]\) and \([u_2v_2w_2]\).

The \((100)\) and \((010)\) planes intersect along \([001]\). The \((100)\) and
\((0\overline{1}0)\) planes, the \((\overline{1}00)\) and \((010)\) planes, the \((\overline{1}00)\) and \((0\overline{1}0)\) planes also
intersect along \([001]\). The \((110)\) and \((\overline{1}10)\) planes also intersect along
\([001]\). Thus their zone axis is \([001]\). The sets of parallel planes in the
\([001]\) zone are \((100), (010), (110)\) and \((\overline{1}10)\). The planes in a given zone
axis can be regarded as forming a two-dimensional lattice.

**Example 1.1** It is known that the faces of an octahedron are \{111\} planes.
The \{111\} planes intersect in triangles with edges along \(<110>\). Find
the angles of the triangles. Find the planes of the \([110]\) zone axis.

**Solution**: Consider the intersection of the \((111)\) face with the \((1\overline{1}1)\) and
\((\overline{1}11)\) faces. The intersection of \((111)\) and \((1\overline{1}1)\) faces is given by

\[
\begin{align*}
[111] \times [1\overline{1}1] &= \begin{vmatrix} i & j & k \\ 1 & 1 & 1 \\ 1 & \overline{1} & 1 \end{vmatrix} = 2\hat{k} - 2\hat{k} = 2[10\overline{1}].
\end{align*}
\]

Similarly the intersection of the \((111)\) and \((\overline{1}11)\) faces is given by

\[
\begin{align*}
\begin{vmatrix} i & j & k \\ 1 & 1 & 1 \\ \overline{1} & 1 & 1 \end{vmatrix} &= -2\hat{j} + 2\hat{k} = 2[0\overline{1}1].
\end{align*}
\]

The angle between the lines \([\overline{1}01]\) and \([0\overline{1}1]\) is given by
\[
\cos^{-1}\left(\frac{1}{\sqrt{2}} \cdot \frac{1}{\sqrt{2}}\right) = \cos^{-1}\left(\frac{1}{2}\right) = 60^\circ.
\]

Thus the \{111\} planes are equilateral triangles.

The zonal equation for the [110] zone axis is: \(h + k = 0\). The planes in the zone are (002), (00\(\bar{2}\)), (1\(\bar{1}\) \(\bar{1}\)), (1\(\bar{1}\) \(\bar{1}\)), (2\(\bar{2}\)0).

## 2. Reciprocal Lattice

### 2.1 1D reciprocal lattice

The set of (100) planes in the [001] zone can be considered as a one-dimensional lattice. The lattice vector is simply \(\vec{a}\), where \(a\) is the spacing between the (100) planes. A reciprocal lattice of the one-dimensional lattice can be defined by a vector \(\vec{a}^*\) perpendicular to the (100) planes with magnitude equal to the inverse of the (100) spacing, i.e. \(a^* = 1/a\).

### 2.2 Basis vectors of 3D reciprocal lattice

The reciprocal lattice, proposed by Ewald, is important for understanding the diffraction of X-ray or electrons by the crystal lattice and useful in the interpretation of diffraction data. The basis vectors of the reciprocal lattice \(\vec{a}^*\), \(\vec{b}^*\) and \(\vec{c}^*\) can be defined in terms of the basis vectors \(\vec{a}\), \(\vec{b}\) and \(\vec{c}\) of the crystal lattice as follows:

\[
\vec{a}^* = \frac{\vec{b} \times \vec{c}}{V_c}, \quad \vec{b}^* = \frac{\vec{c} \times \vec{a}}{V_c}, \quad \vec{c}^* = \frac{\vec{a} \times \vec{b}}{V_c}
\]

where \(V_c = \vec{a} \cdot (\vec{b} \times \vec{c})\) is the volume of the unit cell defined by \(\vec{a}\), \(\vec{b}\) and \(\vec{c}\).

\(\vec{a}^*\) is perpendicular to the \(b\)-\(c\) plane with a “length” equal to the spacing \(\frac{1}{d_{100}}\) of the lattice planes (100). Similarly, \(\vec{b}^*\) is perpendicular to the \(c\)-\(a\) plane with “length” \(\frac{1}{d_{010}}\) and \(\vec{c}^*\) is perpendicular to the \(a\)-\(b\) plane with “length” \(\frac{1}{d_{001}}\).

It can easily be shown that

\[
\vec{a} \cdot \vec{a}^* = 1, \quad \vec{a} \cdot \vec{b}^* = 0, \quad \vec{a} \cdot \vec{c}^* = 0
\]

\[
\vec{b} \cdot \vec{a}^* = 0, \quad \vec{b} \cdot \vec{b}^* = 1, \quad \vec{b} \cdot \vec{c}^* = 0
\]

\[
\vec{c} \cdot \vec{a}^* = 0, \quad \vec{c} \cdot \vec{b}^* = 0, \quad \vec{c} \cdot \vec{c}^* = 1
\]
Using basis vectors \( \bar{a}_1^*, \bar{a}_2^*, \bar{a}_3^* \), the above relationship can be written as
\[
\bar{a}_i \cdot \bar{a}_j^* = \delta_{ij}, \quad i,j = 1, 2, 3.
\]
The reciprocal lattice of the reciprocal lattice is of course the crystal lattice, also termed direct lattice, real lattice.

### 2.3 Reciprocal lattice vector \( \bar{g} \)

A vector \( \bar{g} \) in the reciprocal lattice can be expressed as a linear combination of the basis vectors:
\[
\bar{g} = h\bar{a}^* + k\bar{b}^* + l\bar{c}^*.
\]

1. \( \bar{g} \) is always perpendicular to the lattice plane \((hkl)\). \( \bar{g} \) defines a vector normal to the plane \((hkl)\). Thus each reciprocal lattice point represents a set of lattice planes. (Fig. 1.3)
2. The “length” of the reciprocal lattice vector \( \bar{g} \) is equal to the reciprocal of the lattice plane spacing \( d_{hkl} \). The unit vector normal to the lattice plane \((hkl)\) is \( \hat{n} = \bar{g} / g \). The spacing of the \((hkl)\) plane is given by the projection of the intercept \( \frac{ha}{g}, \frac{kb}{g}, \frac{lc}{g} \) on the unit vector \( \hat{n} \):
\[
d_{hkl} = \hat{n} \cdot \bar{a} = \bar{g} \cdot \bar{a} = \left( \frac{h\bar{a}^* + k\bar{b}^* + l\bar{c}^*}{g} \right) \cdot \bar{a} = \frac{1}{g}.
\]

### 2.4 Lattice plane spacing

Since \( \frac{1}{d_{hkl}^2} = \bar{g} \cdot \bar{g} = h^2|\bar{a}^*|^2 + k^2|\bar{b}^*|^2 + l^2|\bar{c}^*|^2 + 2(h\bar{a}^* \cdot \bar{b}^* + kl\bar{b}^* \cdot \bar{c}^* + lh\bar{c}^* \cdot \bar{a}^*) \)

For orthogonal lattices with \( \bar{a} \perp \bar{b} \perp \bar{c} \) and \( \bar{a}^* \perp \bar{b}^* \perp \bar{c}^* \), this reduces to
\[
\frac{1}{d_{hkl}^2} = h^2|\bar{a}^*|^2 + k^2|\bar{b}^*|^2 + l^2|\bar{c}^*|^2
\]

For a cubic lattice, with \( |\bar{a}^*| = |\bar{b}^*| = |\bar{c}^*| = 1/a \),
\[
d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}.
\]

- Determine the reciprocal lattice corresponding to the lattices in Fig. 1.5 (geometrically and algebraically).

**Example 2.1** A primitive (a) and a centred unit cell (c) are chosen in the same lattice in Fig. 2.1. Construct their respective reciprocal lattice.
Solution: The reciprocal lattices generated with the unit cells of (a) and (c) are given in (b) and (d) in Fig. 2.1. The size of centred unit cell is twice that of the primitive cell. Consequently, the reciprocal lattice generated by the centred cell is twice denser than that obtained from the primitive cell. Note that the unit vectors of the centred cell are mutually perpendicular so that it is easier to generate the reciprocal lattice. On the other hand, the reciprocal lattice of a given lattice must be the same. This will be the case when spots with indices $h+k$ odd (open circles) in (d) are forbidden.

3. Diffraction

Diffraction of a crystal by electrons or X-ray refers to the scattering of the incident waves along well defined directions to a distant plane which is analogous to the optical transform or diffraction (Fraunhofer diffraction). The diffraction pattern is a regular pattern of spots. The discovery of quasicrystals in 1982 has led to the International Union of Crystallography to redefine in 1991 the term “crystal” to mean “any solid having essentially discrete diffraction diagram”. A diffraction pattern of an icosahedral quasicrystal is shown on the front page. Crystals now include “periodic
crystals” which are periodic on the atomic scale and “aperiodic crystals” (or quasicrystals) which are not.

3.1 Optical transform of regularly spaced lines

The optical transform of a set of vertical lines with a regular spacing $d$ is a row of regularly spaced horizontal spots with spacing inversely related to $d$. Rotating the regularly spaced lines into a horizontal position results in a vertical row of spots. The optical transform of a cross grating of regularly spaced lines is a pattern of spots regularly spaced along two perpendicular directions. The spot pattern is the optical analog of the diffraction pattern obtained from a crystal by electron diffraction.

3.2 Bragg Diffraction and Ewald Sphere

When a wave is incident on the periodic array of atoms in a crystal, the waves scattered by the individual atoms interfere to give maximum and minimum intensity in certain definite directions. Consider a wave (X-ray or electron) of wavelength $\lambda$ incident on a set of lattice planes with interplanar spacing $d_{hkl}$ such that the angle between the incident beam and the lattice plane is $\theta$, the scattered wave, also of wavelength $\lambda$, makes the same angle $\theta$ with the lattice plane (Fig. 3.1). For constructive interference, the path difference of rays from successive planes must be an integral multiple of $\lambda$, i.e.

$$2d_{hkl} \sin \theta = n\lambda$$

or $$2d_{hkl} \sin \theta = \lambda$$, where $d_{hkl} = d_{hkl} / n$

which the well known Bragg equation.

![Fig. 3.1](image-url)
The diffraction can also be stated as follows: a diffracted maximum is obtained when the scattering vector $\vec{K}_{hkl}$ is a reciprocal lattice vector $\vec{g}_{hkl}$. The scattering vector is defined as the difference between the scattered wave vector $\vec{k}'$ and the incident wave vector $\vec{k}$, where $|\vec{k}'| = |\vec{k}| = \frac{1}{\lambda}$ and $g_{hkl} = \frac{1}{d_{hkl}}$. Thus

$$\vec{K}_{hkl} = \vec{k}' - \vec{k} = \vec{g}_{hkl}.$$  This is known as the Laue equation.

The Bragg equation and Laue equation are equivalent. The Bragg equation is a real space formulation while the Laue equation is a reciprocal lattice formulation. The Bragg equation can be rewritten as

$$2k\sin\theta = g_{hkl}.$$  The Laue equation can be given a geometrical interpretation due to Ewald (Fig. 3.2). The incident wave vector CO is drawn in the reciprocal lattice of the crystal such that O is on a reciprocal lattice point. The scattered wave vector CG making an angle of $\theta$ with the incident wave vector is next drawn. The Ewald sphere is drawn centred on C and radius CO. For diffraction maximum, G must be a reciprocal lattice point, i.e. OG = $\vec{g}_{hkl}$. In fact, all reciprocal lattice points on the Ewald sphere give diffraction maximum.

From the triangle COM, where M is the midpoint of OG, we have

$$OM = CO \sin\theta$$ or $$g_{hkl} = k\sin\theta$$ which can written as $$\frac{1}{2d_{hkl}} = \frac{1}{\lambda} \sin\theta$$ which gives

$$2d_{hkl} \sin\theta = \lambda,$$  the Bragg equation.
If the reciprocal lattice point is close to, but not on the Ewald sphere, the scattering vector differs from a reciprocal lattice vector by \( s \) so that the Laue equation can be written \( K_{hkl} = \vec{k}' - \vec{k} = \vec{g}_{hkl} + \vec{s} \), where \( s \) is the deviation parameter. The Bragg condition of diffraction is not strictly satisfied, the diffraction intensity is correspondingly reduced.

Consider the X-ray case, typically \( \lambda = 0.1 \text{ nm}, k = 10 \text{ nm}^{-1} \). The scattering angle in a crystal with spacing \( d = 0.5 \text{ nm} \) is about \( 10^0 \). The X-ray Ewald sphere is rather small. Consequently, there can only be a few reciprocal lattice points on the Ewald sphere. This means that it is not so easy to get many diffraction peaks in X-ray diffraction. For 200 kV electrons, \( \lambda = 0.0025 \text{ nm} \) and \( k = 400 \text{ nm}^{-1} \). The corresponding scattering angle in a crystalline plane with spacing \( d = 0.5 \text{ nm} \) is about \( 0.3^0 \). The Ewald sphere in this case is quite large. Consequently the Ewald sphere easily intersect many reciprocal lattice points. It is therefore easy to obtain many diffraction peaks in electron diffraction.

### 3.2 Diffracted Intensity

Bragg’s law deals with the geometry of diffraction. The diffracted intensity \( I_g \) which is the absolute square of the scattered amplitude \( \phi_s \) is dependent on the arrangement of atoms in the diffraction planes. The dependence of \( \phi_s \) on the positions of the atoms in the unit cell and the number as well as the stacking of the unit cells (Fig. 1.1) is given by

\[
\phi_s = \sum_i \sum_n f_i \exp[-2\pi i (\vec{g} + \vec{s}) \cdot (\vec{r}_i + \vec{r}_n)] = \sum_i f_i \exp(-2\pi i \vec{g} \cdot \vec{r}_i) \sum_n \exp(-2\pi i \vec{s} \cdot \vec{r}_n)
\]

where \( f_i \) is the atomic scattering amplitude, \( \vec{r}_i \) denotes the coordinates of the atoms in the unit cell and \( \vec{r}_n \) denotes the location of the unit cell and is thus a lattice vector. The term involving the summation of atoms in the unit cell is known as the structure factor \( F_g \), the term involving the summation of unit cell is known as the shape factor \( G_s \). The diffracted intensity is given by

\[
I_g = |\phi_s|^2 = |F_g|^2 |G_s|^2.
\]

### 3.2.1 Structure Factor

\[
F_{hkl} = \sum_i f_i \exp[-2\pi i (hx + ky + lz)]
\]

(a) Base-centred lattice with two atoms per unit cell at 000 and \( \frac{1}{2} \frac{1}{2} 0 \)
\[ F_{hkl} = f(e^0 + e^{-(h+k)\pi i}) = \begin{cases} 2f, & h+k \text{ even} \\ 0, & h+k \text{ odd} \end{cases} \]

\[ F_{hkl} = 0 \] results in zero intensity or extinction. This is due to the “wrong” choice of a non-primitive unit cell (Example 2.1). The wrong choice results in destructive interference with zero intensity in the unit cell for reflections with \( h + k \) odd. Thus the reciprocal lattice can be obtained by plotting the structure factors.

(b) FCC lattice with four atoms per unit cell at \( 000, \frac{1}{2}\frac{1}{2}0, 0\frac{1}{2}\frac{1}{2} \) and \( \frac{1}{2}\frac{1}{2}\frac{1}{2} \)

\[ F_{hkl} = f(e^0 + e^{-(h+k)\pi i} + e^{-(k+l)\pi i} + e^{-(l+h)\pi i}) = \begin{cases} 4f, & h,k,l \text{ all even or all odd} \\ 0, & h,k,l \text{ mixed} \end{cases} \]

The reciprocal lattice of the FCC lattice obtained by plotting \( F_{hkl} \) for \( hkl \leq 222 \) is shown in Fig. 3.3. It is clear that it is a BCC lattice.

(c) BCC lattice with two atoms per unit cell at \( 000 \) and \( \frac{1}{2}\frac{1}{2}\frac{1}{2} \)

\[ F_{hkl} = f(e^0 + e^{-(h+k+l)\pi i}) = \begin{cases} 2f, & h+k+l \text{ even} \\ 0, & h+k+l \text{ odd} \end{cases} \]

**Example 3.1** List the planes \( (hkl) \) which give diffraction maxima in the BCC and FCC lattices.

**Solution:**

<table>
<thead>
<tr>
<th>((hkl))</th>
<th>(\sqrt{h^2 + k^2 + l^2})</th>
<th>BCC</th>
<th>FCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>(\sqrt{2})</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>111</td>
<td>(\sqrt{3})</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>(\sqrt{4})</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>211</td>
<td>(\sqrt{6})</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>220</td>
<td>(\sqrt{8})</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>310</td>
<td>(\sqrt{10})</td>
<td>x</td>
<td></td>
</tr>
</tbody>
</table>
3.2.2 Shape Factor

Consider a parallelepiped crystal with \( N_1, N_2, N_3 \) unit cells along the crystal axes \( \mathbf{a}, \mathbf{b}, \mathbf{c} \). The dimensions of the crystal are \( N_1 a = L_1, \quad N_2 b = L_2 \) and \( N_3 c = L_3 \). The shape factor is given by

\[
G_s = \sum_m \sum_n \sum_p \exp[-2\pi i (m a_s + n b_s + p c_s)]
\]

since \( \mathbf{r}_n = m \mathbf{a} + n \mathbf{b} + p \mathbf{c} \) and \( \mathbf{s} = s_1 \mathbf{a}_s + s_2 \mathbf{b}_s + s_3 \mathbf{c}_s \).

Now \( \sum_{n=1}^{N_1} \exp(-2\pi i m a_s) = \frac{\sin \pi N_1 a_s}{\sin \pi a_s} \approx \frac{\sin \pi L_1 s_1}{\pi a_s} \)

Therefore

\[
G_s = \frac{\sin \pi L_1 s_1}{\pi a_s} \frac{\sin \pi L_2 s_2}{\pi b_s} \frac{\sin \pi L_3 s_3}{\pi c_s}
\]

Hence

\[
|G_s|^2 = \frac{1}{V_{cell}^2} \left( \frac{\sin \pi L_1 s_1}{\pi s_1} \right)^2 \left( \frac{\sin \pi L_2 s_2}{\pi s_2} \right)^2 \left( \frac{\sin \pi L_3 s_3}{\pi s_3} \right)^2
\]

Each of the factors is of the form \( \left( \frac{\sin \theta}{\theta} \right)^2 \), which is maximum at \( \theta = 0 \) and zero for \( \theta = \pi \). For simplicity, consider a \( L_1 \times L_2 \times L_3 \) orthorhombic crystal

\[
\left( \frac{\sin \pi L_3 s_3}{\pi c s_3} \right)^2 = \begin{cases} (L_3 / c)^2 = N_3^2, & \text{for } s_3 = 0 \\ 0, & \text{for } s_3 = \frac{1}{L_3} \end{cases}
\]

The maximum value is proportional to \((L_3)^2\), the square of the dimension along the crystal axis and falls to zero on both sides. The width is inversely proportional to \( L_3 \). Consequently, the diffracted intensity has strong and narrow peaks for large crystals but weak and broad diffracted intensity distribution for small crystals. The shape factor effect is very important in transmission electron microscopy because specimens in this case are usually thin foils. The reciprocal lattice points become rods in the direction of the electron beam so that they are much more likely to intersect the rather flat Ewald sphere resulting in many diffraction spots. When
precipitates in the form of thin platelets are present in the thin specimen, the shape factor effect will result in reciprocal lattice rods. When the plane of platelets are not perpendicular to the electron beam, streaks are seen in the diffraction pattern.

For example, the presence of thin platelets on (001) plane in a FCC lattice will give rise to reciprocal lattice rods along [001] (Fig. 3.4). View along [001], these rods will intersect the Ewald sphere even when the reciprocal lattice points are not exactly on the sphere, but no streaks are observed. However, when view along [100] or [110], streaks along [001] will be visible.

3.3 Diffraction Patterns

3.3.1 Single Crystal

We shall first consider electron diffraction from single crystals since what is polycrystalline to X-ray is single crystal to electrons since each minute crystal can be probed individually with a small electron beam. The experimental set up for recording the diffraction pattern is shown schematically in Fig. 3.5. The incident beam and each diffraction beam give a diffraction spot on a flat film at a distance of $L$ from the specimen. A flat film is used because the curvature of the Ewald sphere is usually
neglected in electron diffraction. For a diffracted spot at a distance of \( r \) from the central spot due to the incident beam, we have, \( \frac{r}{L} = \tan 2\theta \).

The Bragg equation gives \( 2d_{hkl} \sin \theta = \lambda \). Now the Bragg angle in electron diffraction is very small so that both the tangent and sine can be approximated by the angle \( \theta \), i.e.

\[
\frac{r}{L} = 2\theta \quad \text{and} \quad 2d_{hkl} \theta = \lambda
\]

eliminating the angle, we have

\[
r_{hkl} = (L\lambda)g_{hkl}
\]

where \( L\lambda \) is known as the camera constant. Each diffraction spot corresponds to a reciprocal lattice point. The diffraction pattern is a mapping of the reciprocal lattice.

**Example 3.2** [110] diffraction pattern of a FCC crystal is given in Fig. 3.6. Index the pattern by taking the ratio of the distance of the diffraction spots from the central 000 spot to that of the nearest spot, 002. Measure and calculate the angle between \( g_{111} \) and \( g_{002} \).

Fig. 3.6

**Solution:** First find the vector perpendicular to both [200] and [110] which is given by their cross product \([200] \times [110] = [\overline{2}20]\). The rest of the spots can be obtained by vector addition of [200] and [\overline{2}20].

**Example 3.3** Two sets of coherent thin plates precipitated on the \{111\} planes of an aluminium alloy (FCC) are seen edge-on in a [110] image (Fig. 3.7a). The [110] diffraction pattern is shown in Fig. 3.7b.
There are two sets of short line segments in Fig. 3.7a. The angle between the two sets of line segments is about 70°. Local regions which are slightly bent such that they satisfy the diffraction conditions locally appear dark. Two sets of streaks linking strong diffraction spots due to Al are clearly visible in the associated [110] diffraction pattern in Fig. 3.7b. The angle between the streaks is the same as that between the line segments in Fig. 3.7a. The strong Al spots can readily be indexed as in Example 3.2. The streaks are thus in the direction of the diffraction vectors $\bar{g}_{111}$ and $\bar{g}_{111}$. It is inferred that the streaks which are perpendicular to the $(1\bar{1}1)$ and $(\bar{1}11)$ planes are reciprocal lattice rods rising from the shape factor of line segments which are thin precipitates on $(1\bar{1}1)$ and $(\bar{1}11)$ planes. In addition, the weak spots from the precipitates present at “one-third” positions between the strong Al spots means that the precipitated thin plates are coherent with the Al matrix.

### 3.3.2 Polycrystal

If the diffraction pattern in Fig. 3.6 is rotated about a vertical axis through the central spot, a ring pattern will be obtained. The same pattern will also be obtained by rotating the crystal about the incident beam.
direction. The diffraction pattern from a large number of randomly oriented small crystals forming a polycrystalline solid is a pattern of discontinuous spotty diffraction rings. A ring pattern from passivated nanoparticles if iron is shown in Fig. 3.8. The spotty rings are from iron while the continuous ring is due to passive oxide films on the iron particles.

Fig. 3.8

Structural information can be deduced from the ratios of the radii of the diffraction rings. The radii of the outer rings are usually normalized by dividing by the radius of the first ring. The case of a cubic crystal is quite simple.

\[
\frac{r_j}{r_i} = \frac{\sqrt{h_j^2 + k_j^2 + l_j^2}}{\sqrt{h_i^2 + k_i^2 + l_i^2}}.
\]

The case of powder (aggregate of randomly oriented small crystals) X-ray diffraction is different because the Bragg angles are much larger so that the recording film must follow the curvature of the Ewald sphere. The diffracted beams are recorded by either a circular film or a X-ray detector on a circular track. Here the important parameter is the Bragg angle. And the ratios of the Bragg angles are tabulated. For a cubic crystal,

\[
\sin \theta = \frac{\lambda}{2a} \sqrt{h^2 + k^2 + l^2}, \quad \text{and} \quad \frac{\sin \theta_j}{\sin \theta_i} = \frac{\sqrt{h_j^2 + k_j^2 + l_j^2}}{\sqrt{h_i^2 + k_i^2 + l_i^2}}.
\]

3.3.3 Symmetry of zone axis diffraction pattern

Diffraction patterns taken from a zone axis shows the symmetry of that zone axis. As shown in Fig. 1.5, the symmetry of the cubic (001), (101) and (111) planes is respectively 4mm, 2mm and 6mm. The symmetry of the [101] diffraction pattern as shown in Fig. 3.6 is indeed 2mm. Likewise, the symmetry of a [001] and [111] diffraction pattern is respectively 4mm and 6mm (Fig. 3.9).
However, the symmetry of a <111> zone axis need not be the same as that of a (111) plane. Taking the stacking of (111) planes along a cubic <111> zone axis into consideration, the symmetry of the <111> zone axis is 3m, which is lower than the 6mm symmetry of the (111) plane. Electron diffraction gives the projected symmetry rather than true symmetry of a zone axis.

Fig. 3.9

We shall show below that the true symmetry of a zone axis can be obtained by convergent beam electron diffraction. Symmetry is an intrinsic property of a crystal. The symmetry of zone axis diffraction provides a convenient way for the identification of a crystal orientation and hence the crystal being studied.

4. Obtaining a zone axis diffraction pattern

4.1 Selected area diffraction (SAD) pattern

It is important to correlate the diffraction pattern to a particular feature or area in the image. This is accomplished by selected area diffraction. First an area of interest is chosen in the image with a selected-area diffraction aperture in the image plane. Diffraction from the area chosen is viewed in the diffraction mode. Normally, the crystal is randomly oriented so that a general asymmetrical diffraction pattern obtained is not very useful. The desired crystal orientation is a high symmetry zone axis. Thus we look for a high symmetry zone axis by tilting the crystal in a double-tilt or tilt-rotate stage through a fairly large angle, say 30°. The stage is first set at the eucentric height so that the feature of interest in the crystal remain in place when the crystal is tilted through a large angle. The tilting is then repeated in the diffraction mode. Note how the diffraction pattern changes as the crystal is tilted, especially on approaching a major low-index symmetry axis. Fig. 4.1(a) shows a circular arc of diffraction spots. The radius of the circular arc becomes smaller as the crystal is tilted towards a zone axis, in this case a [110] zone axis, Fig. 4.1(b).
4.2 **Kikuchi diffraction pattern**

Diffraction patterns obtained from a relatively thick and perfect crystal often contain lines in addition to spots. When the thickness of the crystal increases, the spots and lines give way to bands. A Kikuchi pattern close to the [001] zone axis is shown in Fig. 4.2. Kikuchi lines are obtained from the Bragg diffraction of inelastically scattered electrons in a thick crystal. A pair of Kikuchi lines arise from each diffraction plane \((hkl)\). The line closer to the incident beam is dark (deficient line) and the line further away is bright (excess line). When the \(g(hkl)\) line passes through the diffraction spot \((hkl)\), \(s_g = 0\) and the \(\bar{g}\) line passes through \((000)\). If the incident beam is parallel to the diffraction plane, the \(g\) and \(\bar{g}\) Kikuchi line pair are symmetrically placed about \((000)\), passing through the mid points of \(g\) and \(\bar{g}\). When the crystal is tilted slightly, the intensity of diffraction spots is changed, the corresponding Kikuchi lines move substantially, sweeping across the spot diffraction pattern. Thus the Kikuchi pattern is very sensitive to crystal orientation. A zone axis Kikuchi pattern also shows the symmetry of the zone axis.

4.3 **Convergent-beam electron diffraction**

In selected-area diffraction, the incident electron illumination is nearly parallel, the more parallel the electron beam, the sharper are the diffraction spots. The smallest area from which reliable diffraction information can be obtained, limited by the spherical aberration of the objective lens, is about \(0.5 \, \mu m\). In general, the diffraction information is averaged over the thickness and orientation variation of the area which gives rise to the diffraction pattern. When an area in a crystal is probed by a convergent beam of incident electrons, a disk rather a spot diffraction pattern is obtained. When a small probe is used, \(10 – 100 \, nm\), the averaging due to thickness and orientation variation in the probed area is very small, as a result, fringes containing a wealth of useful information of the crystal appear in the diffraction disks. Crystal symmetry, specimen thickness and
lattice parameters can be determined accurately from convergent beam electron diffraction (CBED) patterns. A CBED zone axis pattern of a NbSe$_3$ crystal is shown in Fig. 4.3. The diffraction disks lie within circular and annular bands known as Laue zones. The central zone is the zeroth order Laue zone (ZOLZ) and the rest of the annular bands are collectively called higher-order Laue zones (HOLZs). The first annular band is the first order Laue zone (FOLZ). The symmetry as shown by the ZOLZ reflections is 2mm, with two orthogonal mirror planes perpendicular to the plane of the pattern. But when the symmetry of the FOLZ reflections is taken into consideration, the symmetry is reduced to m. Only the perpendicular plane running across the page is a true mirror plane.

Fig. 4.3

Usually, the diffraction pattern obtained by SAD does not show the HOLZ reflections. Crystallographic information from the third dimensional is lost and a two-dimensional (2D) diffraction pattern is obtained. As a result, the 2-fold rotation axis is always present in the SAD zone axis diffraction patterns. The 10 two-dimensional diffraction point groups degenerate into 6 diffraction point groups. On the other hand, CBED patterns contains 3D crystallographic information. It is possible to deduce the presence of inversion centre ($2_R$), horizontal mirror ($1_R$) (mirror in the plane of the specimen) and horizontal 2-fold axis ($m_R$) from CBED zone axis patterns. Taking the symmetry of the dark-field disks into consideration, a total of 31 diffraction point groups can be obtained. The 31 diffraction point groups are related to the 32 crystal point groups. The 31 diffraction groups are isomorphic to the 31 black and white plane Shubnikov figures or patterns. A polar group corresponds to a pattern with a black surface on one side and a white surface on the other side. The group of horizontal mirror ($1_R$) corresponds to a grey pattern in which the black and white colour of the opposite surface are mixed. Patterns with a vertical 1-fold axis, a horizontal mirror $1_R$, a horizontal 2-fold axis ($m_R$), 2-fold axis, an inversion centre ($2_R$), and $2_Rmm_R$ symmetry are shown in Fig. 4.4.
4.4 Symmetry of CBED zone axis patterns

The symmetry of zone axis diffraction patterns has been summarized by Buxton, Eades, Steeds and Rackham (Phil. Trans. Roy Soc. 281 (1976) 171-194). The symmetry of each of the 31 diffraction groups has been tabulated. For a given zone axis, an on-axis CBED pattern shows the bright field and whole pattern symmetry. The symmetry of a particular dark-field is obtained by slightly tilting the thin crystal to set that dark-field (g) in exact Bragg diffraction. This is then repeated for the dark-field on the opposite side (-g). The symmetry between the ±g (dark-fields) can then be deduced. The procedure is illustrated by the Si <111> patterns in Fig. 4.5.

Note the presence of coarse and fine fringes in the diffraction disks. The coarse fringes are ZOLZ fringes while the fine fringes are HOLZ lines. The ZOLZ fringes are related to the specimen thickness. This is the basis of accurate determination of specimen thickness by CBED. The symmetry obtained by ignoring the fine HOLZ lines is the projected symmetry. <111> bright-field and whole pattern symmetry shown by the 000 pattern are both 3m. The projection symmetry is 6mm. The symmetry of 220 and 220 dark-fields are m. Their projection symmetry is 2mm. The symmetry between the 220 and 220 dark-fields is 2_R which indicates the presence of an inversion centre.
This gives the diffraction group $6_{\text{R}}\text{mm}_{\text{R}}$. The corresponding crystal point groups are $\text{m3m}$ (cubic) and $\overline{3}m$ (trigonal).

The symmetry is also clearly displayed in large angle CBED patterns shown in Fig. 4.6.

![Fig. 4.6](image)

Very often, three patterns from a single zone axis is sufficient to determine or identify the crystal symmetry uniquely. CBED is a very powerful technique for the determination of crystal symmetry and identification of crystal orientation.