Introduction to Reciprocal Space

Master of Crystallography and Crystallization – 2013

T01 – Mathematical, Physical and Chemical basis of Crystallography
The crystallographer’s world view

Reality can be more complex!
Crystals are regular periodic arrays, i.e. they have long range translational symmetry. Crystals are often considered to have essentially infinite dimensions.

**Unit cell** = The smallest volume from which the entire crystal can be constructed by translation only. All crystals have translational symmetry, with the translational vectors equal to edges of the unit cell.

For example, \(a=94.2\,\text{Å}, \ b=72.6\,\text{Å}, \ c=30.1\,\text{Å}, \ \alpha=90^\circ, \ \beta=102.1^\circ, \ \gamma=90^\circ\).
The Reduced Cell

- 3 shortest non-coplanar translations
- Main Conditions (shortest vectors)
- Special Conditions (unique)

- May not exhibit the true symmetry
Because crystals are usually anisotropic (their properties differ along different directions) it is useful to regard a crystalline solid as a collection of parallel planes of atoms. Crystallographers and CM physicists use a shorthand notation (Miller indices) to refer to such planes.

1. Determine intercepts \((x, y, z)\) of the plane with the coordinate axes
Miller Indices, cont’d.

2. Express the intercepts as multiples of the base vectors of the lattice

In this example, let’s assume that the lattice is given by: \( \bar{a} = 1 \hat{i} \quad \bar{b} = 1 \hat{j} \quad \bar{c} = 3 \hat{k} \)

Then the intercept ratios become:

\[
\frac{x}{a} = \frac{1}{1} = 1 \quad \frac{y}{b} = \frac{2}{1} = 2 \quad \frac{z}{c} = \frac{3}{3} = 1
\]

3. Form reciprocals:

\[
\frac{a}{x} = \frac{1}{1} = 1 \quad \frac{b}{y} = \frac{1}{2} \quad \frac{c}{z} = \frac{1}{1} = 1
\]

4. Multiply through by the factor that allows you to express these indices as the lowest triplet of integers:

\[
2 \times (1 \frac{1}{2} 1) = (212)
\]

We call this the (212) plane.
Another example

Find the Miller indices of the shaded plane in this simple cubic lattice:

Intercepts: \( x = \infty \quad y = a \quad z = \infty \) non-intersecting \( \rightarrow \) intercept at \( \infty \)

Intercept ratios: \( \frac{x}{a} = \infty \quad \frac{y}{a} = 1 \quad \frac{z}{a} = \infty \)

Reciprocals: \( \frac{a}{x} = 0 \quad \frac{a}{y} = 1 \quad \frac{a}{z} = 0 \) We call this the \((010)\) plane.

Note:

\((hkl) = \text{a single plane}; \{hkl\} = \text{a family of symmetry-equivalent planes}\)
Crystal Planes and Directions

Crystal directions are specified \([hkl]\) as the coordinates of the lattice point closest to the origin along the desired direction:

Note: \([hkl]\) = a specific direction; \(<hkl>\) = a family of symmetry-equivalent directions

Note that for cubic lattices, the direction \([hkl]\) is perpendicular to the (hkl) plane
Reciprocal Lattice

Unit cell: \( \mathbf{a}, \mathbf{b}, \mathbf{c} \)

Reciprocal lattice unit cell: \( \mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^* \) defined by:

\[
\mathbf{V} = (\mathbf{a} \times \mathbf{b}) \cdot \mathbf{c}
\]

\[
|\mathbf{c}^*| = \frac{|\mathbf{a} \times \mathbf{b}|}{V} = \frac{(\text{area of parallelogram OACB})}{(\text{area of parallelogram OACB})(\text{height of cell})} = \frac{1}{OP} = \frac{1}{d_{001}}
\]

\[
\mathbf{a}^* = \frac{1}{V} \left( \mathbf{b} \times \mathbf{c} \right)
\]

\[
\mathbf{b}^* = \frac{1}{V} \left( \mathbf{c} \times \mathbf{a} \right)
\]

\[
\mathbf{c}^* = \frac{1}{V} \left( \mathbf{a} \times \mathbf{b} \right)
\]

\[
\mathbf{a} \cdot \mathbf{b} = ab \cos \alpha
\]

\[
\mathbf{a} \times \mathbf{b} = ab \sin \alpha
\]
Definition of Reciprocal Lattice Base Vectors

These reciprocal lattice base vectors are defined:

\[ \mathbf{a}^* = \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})} \quad \mathbf{b}^* = \frac{\mathbf{c} \times \mathbf{a}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})} \quad \mathbf{c}^* = \frac{\mathbf{a} \times \mathbf{b}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})} \]

Which have the simple dot products with the direct-space lattice vectors:

\[ \mathbf{a}^* \cdot \mathbf{a} = \mathbf{b}^* \cdot \mathbf{b} = \mathbf{c}^* \cdot \mathbf{c} = 1 \]

\[ \mathbf{a}^* \cdot \mathbf{b} = \mathbf{a}^* \cdot \mathbf{c} = 0 = \mathbf{b}^* \cdot \mathbf{c} = \mathbf{b}^* \cdot \mathbf{a} = \mathbf{c}^* \cdot \mathbf{a} = \mathbf{c}^* \cdot \mathbf{b} \]

\[ \mathbf{G}_{hkl} = h \mathbf{a}^* + k \mathbf{b}^* + l \mathbf{c}^* \]

So compare, for example: \( \omega T = 2\pi n \)

* frequency \( \leftrightarrow \) time

* Reciprocal lattice \( \leftrightarrow \) direct lattice
Reciprocal Lattice

Like the real-space lattice, the reciprocal space lattice also has a translation vector, $H_{hkl}$:

$$H_{hkl} = h\hat{a}^* + k\hat{b}^* + l\hat{c}^*$$

Where the length of $H_{hkl}$ is equal to the reciprocal of the spacing of the $(hkl)$ planes

$$H_{hkl} = |H_{hkl}| = \frac{1}{d_{hkl}}$$

Consider planes of a zone (i.e.: 2D reciprocal lattice).
Planes could be translated so as not to intersect at a common point.
Reciprocal Lattice

\[ \vec{c}^* \perp \vec{a} \quad \vec{c}^* \perp \vec{b} \quad \therefore \vec{c}^* \cdot \vec{a} = \vec{c}^* \cdot \vec{b} = 0 \]

\[ \vec{c}^* \cdot \vec{c} = \left( \frac{1}{OP} \right) OP = 1 \]

\[ \vec{m} \cdot \vec{n}^* = 1, \quad \text{if } m = n, \]

\[ = 0, \quad \text{if } m \neq n. \]

\[ m, n = a, b, c \]

\[ \mathbf{H} \cdot \mathbf{AB} = \left( h \vec{a}^* + k \vec{b}^* + l \vec{c}^* \right) \cdot \left( \frac{\vec{b}}{k} - \frac{\vec{a}}{h} \right) \]

\[ \mathbf{H} \cdot \mathbf{AC} = \left( h \vec{a}^* + k \vec{b}^* + l \vec{c}^* \right) \cdot \left( \frac{\vec{c}}{k} - \frac{\vec{a}}{h} \right) \]

\[ \mathbf{H}_{hkl} = \left( h \vec{a}^* + k \vec{b}^* + l \vec{c}^* \right) \]

Zone axis = \( u \vec{a} + v \vec{b} + w \vec{c} \)

\[ \left( u \vec{a} + v \vec{b} + w \vec{c} \right) \cdot \left( h \vec{a}^* + k \vec{b}^* + l \vec{c}^* \right) = 0 \]

\[ hu + kv + lw = 0 \]
The Reciprocal Lattice

Crystal planes (hkl) in the real-space or direct lattice are characterized by the normal vector $\vec{n}_{hkl}$ and the interplanar spacing $d_{hkl}$:

Long practice has shown the usefulness of defining a different lattice in reciprocal space whose points lie at positions given by the vectors

$$\vec{G}_{hkl} \equiv \frac{\vec{n}_{hkl}}{d_{hkl}}$$

This vector is parallel to the [hkl] direction but has magnitude $1/d_{hkl}$, which is a reciprocal distance.
Consider the three vectors, \( \mathbf{p}_1, \mathbf{p}_2, \) and \( \mathbf{p}_3 \)

\[
\mathbf{p}_1 = \frac{1}{h} \mathbf{a} - \frac{1}{k} \mathbf{b}
\]

\[
\mathbf{p}_2 = \frac{1}{k} \mathbf{b} - \frac{1}{l} \mathbf{c}
\]

\[
\mathbf{p}_3 = \frac{1}{l} \mathbf{c} - \frac{1}{h} \mathbf{a}
\]

Since they are parallel to the plane, the cross product of any two is normal (perpendicular) to the plane.

\[
\mathbf{n} = \mathbf{p}_1 \times \mathbf{p}_2
\]

\[
= \frac{1}{hk} \mathbf{a} \times \mathbf{b} + \frac{1}{kl} \mathbf{b} \times \mathbf{c} + \frac{1}{lh} \mathbf{c} \times \mathbf{a}
\]
If we find the unit normal, $\mathbf{n}/|\mathbf{n}|$, and take its dot product with any vector, $\mathbf{t}$, that terminates on the plane, we get the interplanar distance, $d_{hkl}$.

We can also take the dot products of a pair of these normals to determine the angle between the normals.

Computationally this is not that easy, unless the crystal axes are all orthogonal, so we take a different approach.
Orthorhombic System

All angles are 90°, so the cross products are easily calculated.

\[ \mathbf{a} \times \mathbf{b} = abk \quad \mathbf{b} \times \mathbf{c} = bci \quad \mathbf{c} \times \mathbf{a} = acj \]

and

\[ \mathbf{n} = \frac{bc}{kl} \mathbf{i} + \frac{ac}{hl} \mathbf{j} + \frac{ab}{hk} \mathbf{k} \]

\[ |\mathbf{n}| = \sqrt{\left(\frac{bc}{kl}\right)^2 + \left(\frac{ac}{hl}\right)^2 + \left(\frac{ab}{hk}\right)^2} \]
Orthorhombic System

Now take the simplest vector that terminates on the plane:

\[ \mathbf{t} = \frac{a}{h} \mathbf{i} \]

\[
\vec{t} \cdot \vec{n} = \frac{abc}{hkl}
\]

\[
= \sqrt{\frac{(bc)^2}{kl} + \frac{(ac)^2}{hl} + \frac{(ab)^2}{hk}}
\]
Orthorhombic System

Simplifying and squaring

\[ d_{hkl}^2 = \frac{1}{\left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2} \]
Let’s look back at our normal to the plane equation

\[ n = \frac{1}{hk} \mathbf{a} \times \mathbf{b} + \frac{1}{kl} \mathbf{b} \times \mathbf{c} + \frac{1}{lh} \mathbf{c} \times \mathbf{a} \]

Multiply by \( hkl \)

\[ hkl \mathbf{n} = l \mathbf{a} \times \mathbf{b} + h \mathbf{b} \times \mathbf{c} + k \mathbf{c} \times \mathbf{a} \]

\[ = h \mathbf{b} \times \mathbf{c} + k \mathbf{c} \times \mathbf{a} + l \mathbf{a} \times \mathbf{b} \]

Divide by the volume

\[ \frac{hkl}{V} \mathbf{n} = h \frac{\mathbf{b} \times \mathbf{c}}{V} + k \frac{\mathbf{c} \times \mathbf{a}}{V} + l \frac{\mathbf{a} \times \mathbf{b}}{V} \]
Consider just the last term of this equation with, \( h=0, \ k=0, \ l = 1 \).

\[
\frac{\mathbf{a} \times \mathbf{b}}{V}
\]

\( \mathbf{a} \times \mathbf{b} \) is just a vector perpendicular to the \( ab \) face with length equal to the surface area contained in the \( ab \) face. So...

\[
\frac{\mathbf{a} \times \mathbf{b}}{V} = \frac{1}{d_{001}} = \frac{absen\gamma}{(absen\gamma)c \cos \alpha}
\]
This is a useful result and from it two quantities can be identified, a reciprocal cell spacing, \( c^* \), and a reciprocal lattice spacing, \( d_{001}^* \). These two quantities have units of reciprocal Ångstoms.

\[
c^* = d_{001}^* = \frac{1}{d_{001}} = \frac{a \times b}{c \cdot a \times b}
\]

And we can also define

\[
a^* = d_{100}^* = \frac{1}{d_{100}} = \frac{b \times c}{a \cdot b \times c}
\]

\[
b^* = d_{010}^* = \frac{1}{d_{010}} = \frac{c \times a}{b \cdot c \times a}
\]
Useful Relationships

\[ \mathbf{c}^* \cdot \mathbf{c} = \mathbf{c}^* \mathbf{c} \cos \phi \]

By definition

\[ \mathbf{c}^* = \frac{1}{d_{001}} \]

So

\[ d_{001} = \mathbf{c} \cos \phi \]

By geometry

And by analogy

\[ \mathbf{a}^* \cdot \mathbf{a} = 1 \quad \mathbf{b}^* \cdot \mathbf{b} = 1 \]
**Additional Useful Relationships**

Because by definition a reciprocal space axis is perpendicular to two of the other real space axes, the following are true.

\[ a^* \cdot b = 0 \]
\[ a^* \cdot c = 0 \]
\[ b^* \cdot a = 0 \]
\[ b^* \cdot c = 0 \]
\[ c^* \cdot a = 0 \]
\[ c^* \cdot b = 0 \]
These new **reciprocal lattice axes** can be used to define reciprocal latticed vectors, hkl, just as our regular basis set can be used to define translation vectors, UVW.

\[ \mathbf{d}_{hkl}^* = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \]

In fact the similarities extend to our calculations of distances and angles:

\[ \mathbf{d}_{hkl}^* \cdot \mathbf{d}_{hkl}^* = \left| \mathbf{d}_{hkl} \right| \left| \mathbf{d}_{hkl} \right| \cos \delta = \frac{1}{d_{hkl}^2} \]

\[ \cos \delta = \frac{\mathbf{d}_{hkl_1}^* \cdot \mathbf{d}_{hkl_2}^*}{\left| \mathbf{d}_{hkl_1}^* \right| \left| \mathbf{d}_{hkl_2}^* \right|} \]
The reciprocal lattice is composed of all points lying at positions $\vec{G}_{hkl}$ from the origin, so that there is one point in the reciprocal lattice for each set of planes (hkl) in the real-space lattice.

This seems like an unnecessary abstraction. What is the payoff for defining such a reciprocal lattice?

1. The reciprocal lattice simplifies the interpretation of x-ray diffraction from crystals

2. The reciprocal lattice facilitates the calculation of wave propagation in crystals (lattice vibrations, electron waves, etc.)
Construction of Reciprocal Lattice

1. Identify the basic planes in the direct space lattice, i.e. (001), (010), and (001).

2. Draw normals to these planes from the origin.

3. Mark distances from the origin along these normals proportional to the inverse of the distance from the origin to the direct space planes.
Above a monoclinic direct space lattice is transformed (the b-axis is perpendicular to the page). Note that the reciprocal lattice in the last panel is also monoclinic with $\beta^*$ equal to $180^\circ - \beta$.

The symmetry system of the reciprocal lattice is the same as the direct lattice.
Reciprocal Metric Tensor

The reciprocal metric tensor exists and is defined in an analogous manner to the direct space metric tensor.

\[
G^* = \begin{bmatrix}
a^2 & ab \cos \gamma^* & ac \cos \beta^*
b^* \cos \gamma^* & b^2 & b^* \cos \alpha^*
a^* \cos \beta^* & b^* \cos \alpha^* & c^2
\end{bmatrix}
\]

The good news is that \( G^* \) can be recovered from \( G \):

\[
G^* = G^{-1}
\]
Using the reciprocal metric tensor makes calculation of d-spaces remarkably easy.

\[
\frac{1}{d_{hkl}^2} = \begin{bmatrix} h & k & l \end{bmatrix} G^* \begin{bmatrix} h \\ k \\ l \end{bmatrix}
\]

And also interplanar angles:

\[
\cos \rho = \frac{\left( (h \ k \ l)_1 \right) G^* \left( \begin{bmatrix} h \\ k \\ l \end{bmatrix}_2 \right)}{d_{hkl_1}^* d_{hkl_2}^*}
\]
Calcite Example

Trigonal

\[ a = 4.990 \text{Å}, \; c = 17.061 \text{Å} \]

\[ a^* = b^* = \frac{1}{a \cos \gamma} = 0.23140 \text{Å} \]

\[ c^* = \frac{1}{c} = 0.058613 \text{Å} \]

\[
G^* = \begin{bmatrix}
0.053546 & 0.026773 & 0 \\
0.026773 & 0.053546 & 0 \\
0 & 0 & 0.034354
\end{bmatrix}
\]

\[ \bar{3} 2 / m \]
What is the Angle Between (104) and (114)

\[
d_{104}^{*2} = \begin{bmatrix} 1 & 0 & 4 \end{bmatrix} G^* \begin{bmatrix} 0 \\ 0 \\ 4 \end{bmatrix} = 0.108514 \text{Å}^{-2}
\]

\[
d_{104}^* = 0.32941 \text{Å}^{-1} = d_{\overline{1}14}^*
\]

These two spacings are the same because they are related by three-fold symmetry.
Calcite Example (continued)

\[ d_{104}^* \cdot d_{114}^- = \begin{bmatrix} 1 & 0 & 4 \end{bmatrix} G^* \begin{bmatrix} 1 \\ 1 \\ 4 \end{bmatrix} = 0.028195 \text{Å}^{-2} \]

So

\[ \rho = \cos^{-1} \left( \frac{d_{104}^* \cdot d_{114}^-}{|d_{104}^*| |d_{114}^-|} \right) \]

\[ = \cos^{-1} \left( \frac{0.028195}{0.32941 \times 0.32941} \right) \]

\[ = 74.94^\circ \]
Direct Space to Reciprocal Space

\[
\begin{align*}
    a^* &= \frac{bc \sin \alpha}{V} \\
    b^* &= \frac{ca \sin \beta}{V} \\
    c^* &= \frac{ab \sin \gamma}{V} \\
    \cos \alpha^* &= \frac{\cos \beta \cos \gamma - \cos \alpha}{\sin \beta \sin \gamma} \\
    \cos \beta^* &= \frac{\cos \gamma \cos \alpha - \cos \beta}{\sin \gamma \sin \alpha} \\
    \cos \gamma^* &= \frac{\cos \alpha \cos \beta - \cos \gamma}{\sin \alpha \sin \beta} \\
    V^* &= \frac{1}{V} \\
    \frac{\sin \alpha^*}{\sin \alpha} &= \frac{\sin \beta^*}{\sin \beta} = \frac{\sin \gamma^*}{\sin \gamma}
\end{align*}
\]

\[
V^* = a^*b^*c^* \sqrt{1 - \cos^2 \alpha^* - \cos^2 \beta^* - \cos^2 \gamma^* + 2 \cos \alpha^* \cos \beta^* \cos \gamma^*}
\]

\[
V^* = a^*b^*c^* \sin \alpha^* \sin \beta^* \sin \gamma \\
= a^*b^*c^* \sin \alpha^* \sin \beta^* \sin \gamma^* \\
= a^*b^*c^* \sin \alpha^* \sin \beta^* \sin \gamma^*
\]

\[
G^* = \begin{bmatrix}
    a^{*2} & a^*b^* \cos \gamma^* & a^*c^* \cos \beta^* \\
    b^*a^* \cos \gamma^* & b^{*2} & b^*c^* \cos \alpha^* \\
    c^*a^* \cos \beta^* & c^*b^* \cos \alpha^* & c^{*2}
\end{bmatrix}
\]
Reciprocal Space to Direct Space

\[ a = \frac{b^*c^* \sin \alpha^*}{V} \]
\[ b = \frac{c^*a^* \sin \beta^*}{V} \]
\[ c = \frac{a^*b^* \sin \gamma^*}{V} \]
\[ \cos \alpha = \frac{\cos \beta^* \cos \gamma^* - \cos \alpha^*}{\sin \beta^* \sin \gamma^*} \]
\[ \cos \beta = \frac{\cos \gamma^* \cos \alpha^* - \cos \beta^*}{\sin \gamma^* \sin \alpha^*} \]
\[ \cos \gamma = \frac{\cos \alpha^* \cos \beta^* - \cos \gamma^*}{\sin \alpha^* \sin \beta^*} \]
\[ V = \frac{1}{V^*} \]
\[ \frac{\sin \alpha}{\sin \alpha^*} = \frac{\sin \beta}{\sin \beta^*} = \frac{\sin \gamma}{\sin \gamma^*} \]

\[ V = abc \sqrt{1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma} \]
\[ V = abc \sin \alpha \sin \beta \sin \gamma^* \]
\[ V = abc \sin \alpha \sin \beta^* \sin \gamma \]
\[ V = abc \sin \alpha^* \sin \beta \sin \gamma \]

\[ G = \begin{bmatrix}
  a^2 & ab \cos \gamma & ac \cos \beta \\
  ba \cos \gamma & b^2 & bc \cos \alpha \\
  ca \cos \beta & cb \cos \alpha & c^2
\end{bmatrix} \]
Dspace
Equations

Cubic: \[ \frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \]

Tetragonal: \[ \frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \]

Hexagonal: \[ \frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 +hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \]

Rhombohedral: \[ \frac{1}{d^2} = \frac{(h^2 + k^2 + l^2) \sin^2 \alpha + 2(hk + kl + hl)(\cos^2 \alpha - \cos \alpha)}{a^2(1 - 3 \cos^2 \alpha + 2 \cos^3 \alpha)} \]

Orthorhombic: \[ \frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \]

Monoclinic: \[ \frac{1}{d^2} = \frac{1}{\sin^2 \beta} \left( \frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right) \]

Triclinic: \[ \frac{1}{d^2} = \frac{1}{V^2} (S_{11}h^2 + S_{22}k^2 + S_{33}l^2 + 2S_{12}hk + 2S_{23}kl + 2S_{13}hl) \]

In the equation for triclinic crystals,

\[ V = \text{volume of unit cell (see below)}, \]
\[ S_{11} = b^2c^2 \sin^2 \alpha, \]
\[ S_{22} = a^2c^2 \sin^2 \beta, \]
\[ S_{33} = a^2b^2 \sin^2 \gamma, \]
\[ S_{12} = abc^2 (\cos \alpha \cos \beta - \cos \gamma), \]
\[ S_{23} = a^2bc (\cos \beta \cos \gamma - \cos \alpha), \]
\[ S_{13} = ab^2c (\cos \gamma \cos \alpha - \cos \beta). \]
Wigner-Seitz Cell

Form connection to all neighbors and span a plane normal to the connecting line at half distance.
a) Select a lattice point and draw construction lines to the nearest neighboring points.

b) Draw lines that perpendicularly bisect the construction lines.

c) The smallest enclosed area represents the Wigner-Seitz cell. Here shown in orange.
First Brillouin Zone: Two Dimensional Oblique Lattice

Figure 10  Construction of the first Brillouin zone for an oblique lattice in two dimensions. We first draw a number of vectors from $O$ to nearby points in the reciprocal lattice. Next we construct lines perpendicular to these vectors at their midpoints. The smallest enclosed area is the first Brillouin zone.
Real Space

BCCWS cell

Reciprocal Space

BCC BZ

FCC WS cell

FCC BZ
Real and Reciprocal Lattices
The diffraction pattern also forms a lattice

Most contemporary x-ray data collection used the rotation geometry, in which the crystal makes a simple rotation of a degree or so while the image is being collected. The geometry of the diffraction pattern is less obvious than for a precession photograph, although data collection is more efficient.

Oscillation (rotation) photograph.

[Diagram showing X-rays passing through a crystal, which rotates during exposure]
The lattice of diffracted x-rays has an inverse or reciprocal relationship to the crystal lattice. For this reason the lattice of the diffraction pattern is called the reciprocal lattice, while the crystal is said to form the real or direct lattice.

It is important to remember that the crystal lattice, the reciprocal lattice, and Miller planes are not actual physical objects - assuming you could see objects that small, you would not see an actual dot at the corner of a unit cell, etc. Nevertheless, these concepts are extremely helpful for crystal structure determination.
Period Doubling in Reciprocal Space

- Doubling the periodicity in real space produces twice as many diffraction spots in reciprocal space.
- This effect can be produced chemically with an ordered binary alloy or magnetically with antiparallel spins in and antiferromagnet.
- The primitive vectors of the reciprocal lattice are found from:
  \[
  \vec{b}_i = \frac{\vec{a}_j \times \vec{a}_k}{\vec{a}_i \cdot (\vec{a}_j \times \vec{a}_k)}
  \]

- A doubling of the periodicity in real space due to antiferromagnetism will produce half-order spots in reciprocal space.
- The magnetic scattering of neutrons gives them a unique property of scattering from spins in antiferromagnetic ordered structures.
Symmetry of the Diffraction Pattern

The diffraction pattern has almost the same symmetry as the crystal. One important difference is that the diffraction pattern also contains a center of inversion (Friedel symmetry). The combination of rotational symmetry and a center of inversion can give rise to mirror plane symmetry in the diffraction pattern – which of course is not possible in the crystal.

The diffraction pattern loses information about translational symmetry.

Friedel symmetry. This precession photograph is a slice through the center of the reciprocal lattice.
The Ewald Sphere
This means that when a lattice point intersects the Ewald sphere, the reflection corresponding to that family of planes will be observed and the diffraction angle will be apparent. The step-by-step construction and initial use of a Ewald sphere is described on the web site (http://www.doitpoms.ac.uk/tlplib/reciprocal_lattice/ewald.php).

Starting with an indexed reciprocal lattice, an incident X-ray beam must pass through the origin (000) point, corresponding to the direct undiffracted beam of X-rays.
The Ewald sphere for this case is defined by making a sphere of radius \(1/\lambda\) having its diameter on the X-ray beam that intersects the origin point. In the diagram on the left, no other RL points are on the surface of the sphere so the Bragg condition is not satisfied for any of the families of planes. To observe reflections, the reciprocal lattice must be rotated until an RL point contacts the surface of the sphere. **Note:** It would be easier to rotate the sphere on paper, but in practice, we rotate the crystal lattice and the RL.
When a reciprocal lattice point intersects the Ewald sphere, a reflection will occur and can be observed at the $2\theta$ angle of the inscribed triangle. To be able to collect as many different reflections as possible, it is thus necessary to be able to rotate the reciprocal lattice to a great extent...
The Ewald Sphere

Our need to rotate the crystal in numerous ways to bring all of the families of planes into reflection (i.e. to make RL point intersect with the Ewald sphere) explains the design of the goniometer portion of the diffractometer. The 4-circles of the goniometer allows the crystal to be rotated in virtually any direction while remaining in the X-ray beam. The labels for each of the goniometer axes ($\phi$, $\chi$, $\omega$, and $\theta$) are indicated on the diagram below. Note that there are different designs (such as the Kappa geometry) that accomplish the same task.
The Ewald Sphere

If one rotates the Ewald sphere completely about the (000) reciprocal lattice point in all three dimensions, the larger sphere (of radius $2/\lambda$) contains all of the reflections that it is possible to collect using that wavelength of X-rays. This construction is known as the “Limiting sphere” and it defines the complete data set. Any reciprocal lattice points outside of this sphere can not be observed. Note that the shorter the wavelength of the X-radiation, the larger the Ewald sphere and the more reflections may be seen (in theory).

The limiting sphere will hold roughly $(4/3\pi r^3/ V^*)$ lattice points. Since $r = 2/\lambda$, this equates to around $(33.5/ V^*\lambda^3)$ or $(33.5 V/\lambda^3)$ reflections. For an orthorhombic cell with a volume of 1600Å$^3$, this means CuKα can give around 14,700 reflections while MoKα would give 152,000 reflections.
The Ewald Sphere

Remember that the reciprocal lattice can also be defined in terms of the wavelength of the X-radiation (by setting $K = \lambda$). In such a construction, the Ewald sphere remains the same size, having a radius of 1 ($\lambda \cdot 1/\lambda = 1$), independent of the wavelength. Such pictures show the increased number (and density) of reflections for the shorter wavelength radiation. As noted previously, this means that longer wavelength radiation might be necessary to resolve individual reflections for crystals with large unit cells and small reciprocal unit cells.

To see many of these effects, get XrayView (http://phillips-lab.biochem.wisc.edu/software.html).
Fourier Series in XRD

**Fourier series**

Continuous, Periodic $\rightarrow$ Discrete, Aperiodic

**Election Density Distribution** $\rightarrow$ **Structure Factor**

$\rho(x,y,z)$ $\rightarrow$ $F(hkl)$

**Real Space** ($R^3$) $\rightarrow$ **Reciprocal Space** ($Z^3$)
The Nature of F Transform

Re-express a function in one domain into another domain (conjugate domain)

- e.g. Time domain $\rightarrow$ Frequency domain
  - Real space $\rightarrow$ Reciprocal space

Now, to know a function, we have two ways:

(1) **From the original domain**
- directly measure $(x, f(x))$, get enough sample points and do regression. *(can we measure the electron density distribution as we measure water density in a pond?)*

(2) **From the conjugate domain**
- get $C(n)$, and transform to original domain
Fourier Transform pair

In Crystallography

\[ F(h) = \int_V \rho(r) \exp(2\pi i (h \cdot r)) \, dv \]

\[ \rho(r) = \frac{1}{V} \sum_h F(h) \exp(-2\pi i (h \cdot r)) \]

Note

the exponential term, one has a minus sign, the other hasn’t; the period \((V)\) is involved in one equation.
Kevin Cowtan’s Fourier Duck

http://www.ysbl.york.ac.uk/~cowtan/fourier/magic.html
Kevin Cowtan’s Fourier Cat

http://www.ysbl.york.ac.uk/~cowtan/fourier/magic.html
Magnitudes from duck and phases from cat
Magnitudes from cat and phases from duck
A tail of two cats

http://www.ysbl.york.ac.uk/~cowtan/fourier/coeff.html

Magnitudes only
A similar structure – tail-less Manx cat
Despite the fact that the phases contain more structural information about the image than the magnitudes, the missing tail is restored at about half of its original weight. This occurs only when the phases are almost correct. The factor of one half arises because we are making the right correction parallel to the estimated phase, but no correction perpendicular to the phase (and $<\cos 2> = 1/2$). There is also some noise in the image.
“A $2|\text{Fo}| - |\text{Fc}|$ map”
Introduction to Reciprocal Space

Master of Crystallography and Crystallization – 2013

T01 – Mathematical, Physical and Chemical basis of Crystallography

END