The Reciprocal Lattice

These notes are a compilation of material found in *Elements of X-Ray Diffraction*, by B.D. Cullity, *Space Groups for Solid State Scientists*, by Gerald Burns and A.M. Glazer, *Elements of X-Ray Crystallography*, by Leonid V. Azaroff, and *Structure of Metals*, by Charles Barrett and T.B. Massalski.

The reciprocal lattice is a mathematical construction that is used to make various crystallographic and diffraction calculations. While its utility is not obvious when working with cubic crystal systems, it is an invaluable tool when addressing the fine points of x-ray diffraction, working with low-symmetry crystal systems, and solving electron diffraction patterns. It should again be emphasized that a reciprocal lattice does not physically exist.

Review of Vector Operations

Dot product (scalar product)

$$\vec{x} \bullet \vec{y} = |\vec{x}||\vec{y}|\cos\alpha$$

Cross product (vector product:

$$\vec{x} \times \vec{y} = \vec{z} = |\vec{x}||\vec{y}|\sin\alpha$$

where the direction of $\vec{z}$ is normal to the $\vec{x}$- $\vec{y}$ plane,
and the magnitude of $\vec{z}$ is equal to the area of
the parallelogram defined by $\vec{x}$ and $\vec{y}$.

Defining the Reciprocal Lattice

Take an arbitrary lattice ($a \neq b \neq c$ and $\alpha \neq \beta \neq \gamma$ ($\neq 90°$) in real space. We can take advantage of the properties of the cross product and define the reciprocal lattice as follows:

$$\vec{a}^* = \frac{(\vec{b} \times \vec{c})}{\vec{a} \bullet (\vec{b} \times \vec{c})} \quad \vec{b}^* = \frac{(\vec{c} \times \vec{a})}{\vec{b} \bullet (\vec{c} \times \vec{a})} \quad \vec{c}^* = \frac{(\vec{a} \times \vec{b})}{\vec{c} \bullet (\vec{a} \times \vec{b})}$$

where $\vec{a} \bullet (\vec{b} \times \vec{c}) = \vec{b} \bullet (\vec{c} \times \vec{a}) = \vec{c} \bullet (\vec{a} \times \vec{b}) =$ unit cell volume,
and $\vec{a}^*$ is the reciprocal lattice vector for $\vec{a}$ *et cetera.*

Note : in orthogonal real lattices ($\alpha = \beta = \gamma = 90°$),
$\vec{a}^* // \vec{a}$, $\vec{b}^* // \vec{b}$, and $\vec{c}^* // \vec{c}$.

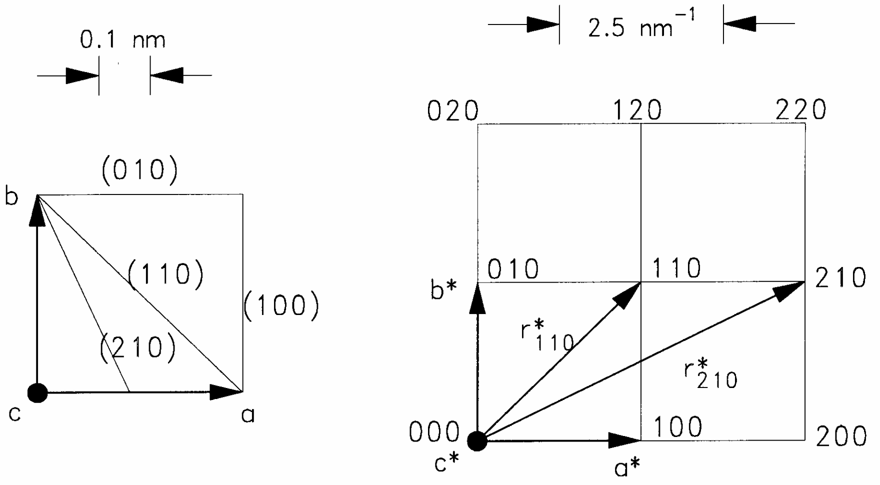
Reciprocal Lattice Construction

The following analogy can be made between the reciprocal and real lattices:

$\vec{r}_{uvw} = u\vec{a} + v\vec{b} + w\vec{c}$ to build a real lattice from unit cells
and
$\vec{r}^*_{hkl} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$ to build a reciprocal lattice

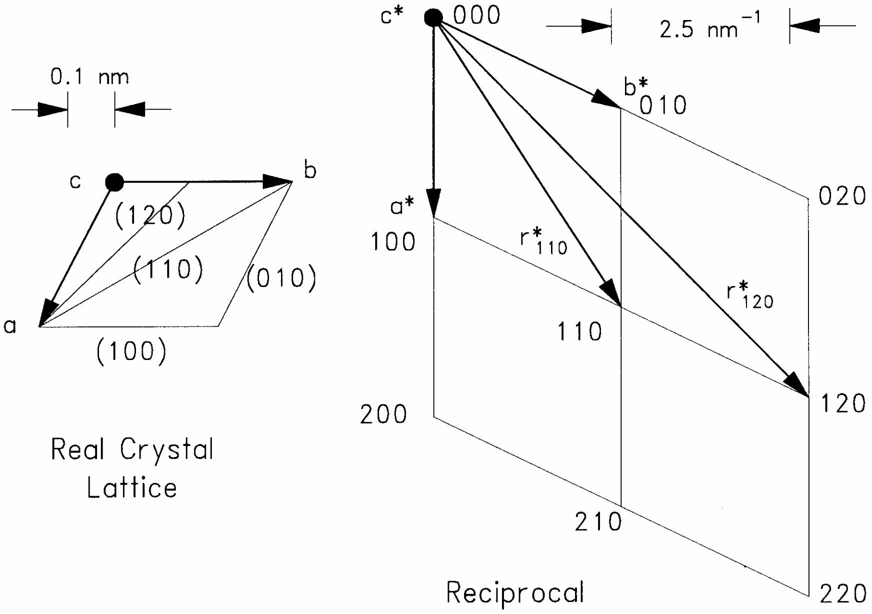
Note that the entire reciprocal lattice is actually taken from only one unit cell.

Sketches of real and reciprocal lattices (both cubic and hexagonal) are shown below. These drawings are modifications of figures in *Cullity* for a cubic and hexagonal lattice with a = 0.4 nm and the c-axis coming out of the page:



Real Crystal Lattice

Reciprocal Lattice



Real Crystal Lattice

Reciprocal Lattice

We can demonstrate one of the useful properties of the reciprocal lattice rather easily:

$$\left|\vec{c}^*\right| = \left|\frac{\left(\vec{a}\times\vec{b}\right)}{\vec{c}\bullet\left(\vec{a}\times\vec{b}\right)}\right|$$

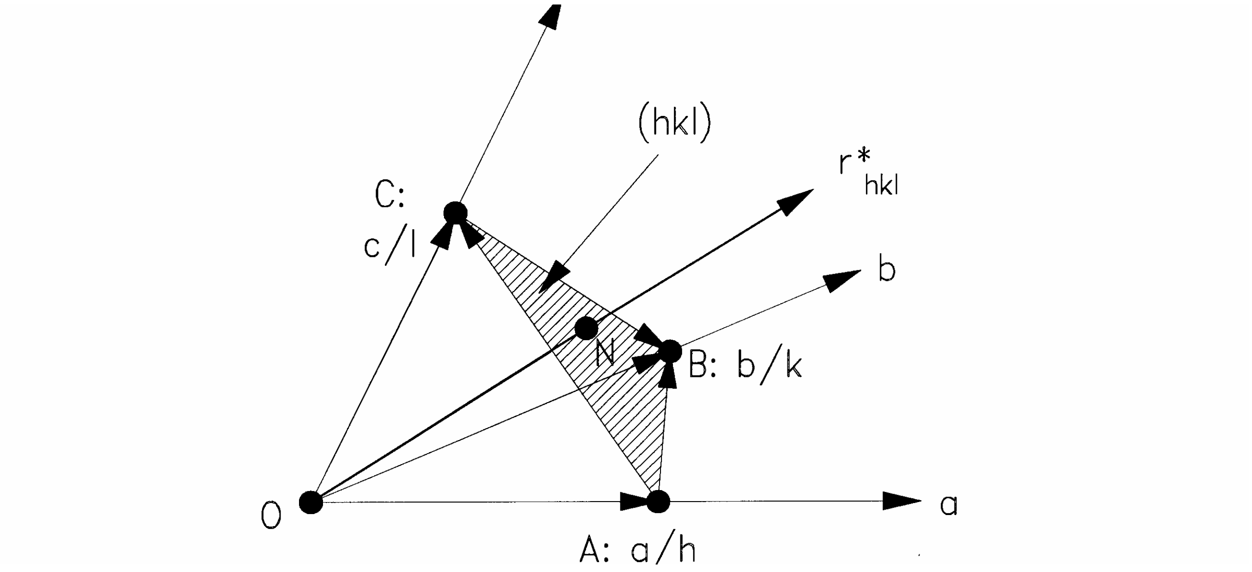
$$= \left|\frac{\text{area of base}}{\text{unit cell volume}}\right|$$

$$= \frac{1}{\text{height}}$$

$$= \frac{1}{d_{001}}$$

<u>Proofs and Derivations</u>

There are several important proofs and derivations that start from the same sketch, also taken from *Cullity.*



Perpendicularity

Prove that the reciprocal lattice vector is normal to the plane (real lattice) of the same indices:

Basis: if a line is perpendicular to two lines in a plane, then it is perpendicular to that plane (yes, this is high school geometry).

$$\overline{AB} = \frac{\vec{b}}{k} - \frac{\vec{a}}{h}$$

$$\overline{BC} = \frac{\vec{c}}{l} - \frac{\vec{b}}{k}$$

Recall: If the dot product of two vectors = 0, then the angle between them is 90°.

$$\vec{r}^*_{hkl} \bullet \overline{AB} = \left(h\vec{a}^* + k\vec{b}^* + l\vec{c}^*\right)\bullet\left(\frac{\vec{b}}{k} - \frac{\vec{a}}{h}\right)$$

$$\text{recall that } \vec{a}^* \bullet \vec{a} = \vec{b}^* \bullet \vec{b} = \vec{c}^* \bullet \vec{c} = 1$$

(Use the definitions to prove this to yourself.)

$$\text{and } \vec{a}^* \bullet \vec{b} = 0 \text{ etc. for all other combinations.}$$

$$\vec{r}^*_{hkl} \bullet \overline{AB} = -\frac{h}{h} + \frac{k}{k}$$

$$= 0$$

$$\text{Similarly, } \vec{r}^*_{hkl} \bullet \overline{BC} = 0$$

Interplanar Spacing

Prove that interplanar spacing = ON = d_{hkl}

$$\text{Unit vector} \perp \text{plane (hkl)} = \frac{r^*_{hkl}}{|r^*_{hkl}|}$$

Recall that a dot product gives the length of the component in the same direction:

$$\cos\alpha = \frac{\text{projected length}}{|\vec{h}|}$$

$$\text{and } \vec{g} \bullet \vec{h} = |\vec{g}||\vec{h}| \cos\alpha$$

$$\text{Therefore, } \vec{g} \bullet \vec{h} = |\vec{g}| \text{ (projected length)}$$

$$\text{Since } |\vec{g}| = 1, \text{ (the definition of a unit vector),}$$

$$\text{then } \vec{g} \bullet \vec{h} = \text{projected length.}$$

Thus:

$$\frac{\vec{r}^*_{hkl}}{|\vec{r}^*_{hkl}|} \bullet \frac{\vec{a}}{h} = \vec{ON} = d_{hkl}$$

$$\frac{h\vec{a}^* + k\vec{b}^* + l\vec{c}^*}{|\vec{r}^*_{hkl}|} \bullet \frac{\vec{a}}{h} = d_{hkl}$$

$$\frac{h}{h} \bullet \frac{1}{|\vec{r}^*_{hkl}|} = d_{hkl}$$

$$\text{The same arguments are valid for } \frac{\vec{b}}{k} \text{ and } \frac{\vec{c}}{l}.$$

Calculation of Interplanar Spacing, d_{hkl}:

We know that $\vec{z} \bullet \vec{z} = |z|^2$.

$$\text{Since } d_{hkl} = \frac{1}{|\vec{r}^*_{hkl}|}, \text{ then:}$$

$$\frac{1}{d^2} = \left(h\vec{a}^* + k\vec{b}^* + l\vec{c}^*\right) * \left(h\vec{a}^* + k\vec{b}^* + l\vec{c}^*\right)$$

$$\frac{1}{d^2} = h^2|\vec{a}^*|^2 + k^2|\vec{b}^*|^2 + l^2|\vec{c}^*|^2 + 2hk|\vec{a}^*||\vec{b}^*|\cos\gamma^* +$$

$$2kl|\vec{b}^*||\vec{c}^*|\cos\alpha^* + 2hl|\vec{a}^*||\vec{c}^*|\cos\beta^*$$

where $\alpha^* = \angle$ between $\vec{b}^*$ and $\vec{c}^*$ etc.

From geometry (and without derivation):

$$\cos\alpha^* = \frac{\cos\beta \ \cos\gamma \ \cos\alpha}{\sin\gamma \ \sin\beta}$$

$$\cos\beta^* = \frac{\cos\alpha \ \cos\gamma \ \cos\beta}{\sin\alpha \ \sin\gamma}$$

$$\cos\gamma^* = \frac{\cos\alpha \ \cos\beta \ \cos\gamma}{\sin\alpha \ \sin\beta}$$

Look at simple cases:

For orthogonal crystals: $\alpha^* = \beta^* = \gamma^* = 90°$

$$\frac{1}{d^2} = h^2|\vec{a}^*|^2 + k^2|\vec{b}^*|^2 + l^2|\vec{c}^*|^2$$

$$= \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

which simplifies further for tetragonal and cubic crystal structures.

Calculate Angle between Planes

Note: In the general case,
$\angle$ between $[h_1k_1l_1]$ and $[h_2k_2l_2] \neq \angle$ between $(h_1k_1l_1)$ and $(h_2k_2l_2)$.

$\therefore$ must use $\vec{r}^*_{h_1k_1l_1}$ and $\vec{r}^*_{h_2k_2l_2}$

$$\vec{r}^*_1 \bullet \vec{r}^*_2 = |\vec{r}^*_2| \ |\vec{r}^*_2| \cos\phi$$

or

$$\cos\phi = \frac{\vec{r}^*_1 \bullet \vec{r}^*_2}{|\vec{r}^*_1| \ |\vec{r}^*_2|} = \vec{r}^*_1 \bullet \vec{r}^*_2 \text{ x } (d_1 \text{ x } d_2)$$

$$\cos\phi = d_1d_2 \bullet \{(h_1\vec{a}^* + k_1\vec{b}^* + l_1\vec{c}^*) \bullet (h_2\vec{a}^* + k_2\vec{b}^* + l_2\vec{c}^*)\}$$

$$\cos\phi = d_1d_2 \text{ x} \Big(h_1h_2|\vec{a}^*|^2 + k_1k_2|\vec{b}^*|^2 + l_1l_2|\vec{c}^*|^2 + (h_1k_2 + h_2k_1)|\vec{a}^*||\vec{b}^*|\cos\gamma^* +$$

$$(h_1l_2 + h_2l_1)|\vec{a}^*||\vec{c}^*|\cos\beta^* + (k_1l_2 + k_2l_1)|\vec{b}^*||\vec{c}^*|\cos\alpha^*\Big)$$

Can simplify for orthogonal systems since cos(90°) = 0:

$$\cos\phi \;=\; d_1 d_2 \left(h_1h_2|\vec{a}^*|^2 \;+\; k_1k_2|\vec{b}^*|^2 \;+\; l_1l_2|\vec{c}^*|^2\right)$$

$$\text{recall that } \frac{1}{d_1} \;=\; \sqrt{\frac{h_1^2}{a^2} + \frac{k_1^2}{b^2} + \frac{l_1^2}{c^2}}$$

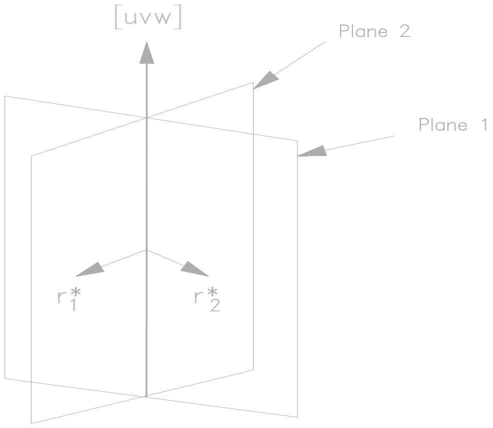
$$\text{and } |\vec{a}^*|^2 \;=\; \frac{1}{a^2} \text{ et cetera.}$$

$$\cos\phi \;=\; \frac{\dfrac{h_1h_2}{a^2} + \dfrac{k_1k_2}{b^2} + \dfrac{l_1l_2}{c^2}}{\sqrt{\dfrac{h_1^2}{a^2} + \dfrac{k_1^2}{b^2} + \dfrac{l_1^2}{c^2}}\;\sqrt{\dfrac{h_2^2}{a^2} + \dfrac{k_2^2}{b^2} + \dfrac{l_2^2}{c^2}}}$$

Determination of Zone Axes

We are often concerned with the zone axis of a given set of planes. A zone axis is defined as "the direction which is common (and parallel) to two or more planes." It is important to note that a plane can be part of an infinite number of zones since it contains and infinite number of lines.

Generally, the direction normal to two planes is given by the cross product of their two normals.



$$\text{Recall that direction}[uvw] = u\vec{a} + v\vec{b} + w\vec{c},$$

$$\text{and that } \vec{r}^*_{hkl} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*.$$

$$\text{If } [uvw] \perp \vec{r}^*_{hkl}, \text{ then } [uvw] \bullet \vec{r}^*_1 = 0, \text{ and}$$

$$hu + kv + lw = 0$$

This is known as the Weiss zone law.

A certain amount of caution must be exercised since we are now concerned with both planes and directions. For example, in hexagonal crystals, the zone axis is calculated by the following equations:

$$u = l_2(2k_1 + h_1) - l_1(2k_2 + h_2)$$

$$v = l_1(2h_2 + k_2) - l_2(2h_1 + k_1)$$

$$w = 3(h_1k_2 - h_2k_1)$$

$$t = -(u + v)$$

Zone axes can be readily determined using a stereographic projection, although the projection must include both planes and directions for non-cubic crystals.

Application of the Reciprocal Lattice to Diffraction

As will be demonstrated below, the necessary conditions for the occurrence of diffraction can be based upon the reciprocal lattice.

To begin, Bragg's Law can be restated as "diffraction, i.e., the constructive interference of waves interacting with a crystal, will occur when the Ewald sphere is in contact with a reciprocal lattice point."

The geometry of diffraction is shown below. Points O and P are the original (000) and hkl of a reciprocal lattice. Vectors are defined as follows:

$$\vec{k} = IO$$
$$= \text{incident beam}$$

$$\vec{k}' = IP$$
$$= \text{diffracted beam}$$

$$\vec{g} = OP$$
$$= \text{reciprocal lattice vector for plane hkl}$$

$$|\vec{k}| = |\vec{k}'| = \frac{1}{\lambda}$$

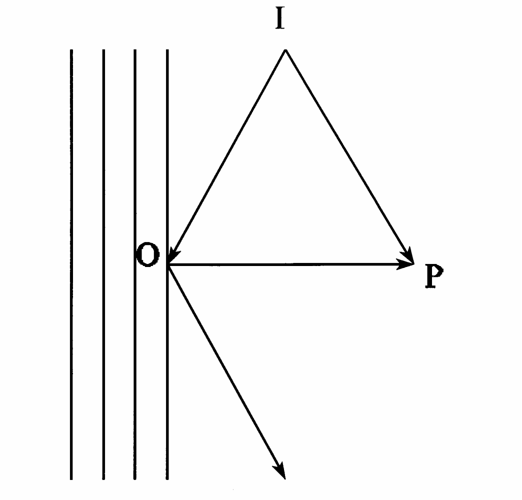
$$|\vec{g}| = \frac{1}{d_{hkl}}$$

$$\angle \vec{k}\vec{k}' = 2\theta$$

$$\text{Since } \vec{k}' = \vec{k} + \vec{g},$$

$$\sin\theta = \frac{\frac{|\vec{g}|}{2}}{|\vec{k}|} = \frac{\frac{1}{2d}}{\frac{1}{\lambda}}, \text{ and}$$

$$\lambda = 2d\sin\theta, \text{ which is Braggs law}$$



The criteria of contact between a reciprocal lattice point and the Ewald sphere is the so-called exact Bragg condition, which is overly restrictive.

The Ewald sphere is particularly useful when applied to electron diffraction since the wavelength of high energy electrons is very small and, therefore, each zone axis is essentially a planar section of the reciprocal lattice. By using typical values for wavelength and lattice spacing, we can demonstrate the "Christopher Columbus Effect". For a 200 kV electron, $\lambda = 0.00251$ nm. For a typical crystal, $d \cong 0.2$ nm and, therefore, $|g| \cong 5\ \text{nm}^{-1}$. Thus, the ratio of the radius to the reciprocal lattice spacing is approximately 80, which approaches a plane.

The definition of a reciprocal lattice does not include any information on the position of atoms within the unit cell. However, structure factor calculations and the reciprocal lattice can be combined to show how electron diffraction patterns emerge. This is accomplished by only placing a reciprocal lattice point when the structure factor (and, therefore, the diffracted intensity) is non-zero. One of the curious coincidences which result from this method is that the reciprocal lattice of a face-centered crystal is body centered and vice versa. It should also be noted that the symmetry of the crystal (real space) is carried over into reciprocal space. For example, a {111} zone axis for a cubic crystal has three-fold symmetry in both real and reciprocal space.