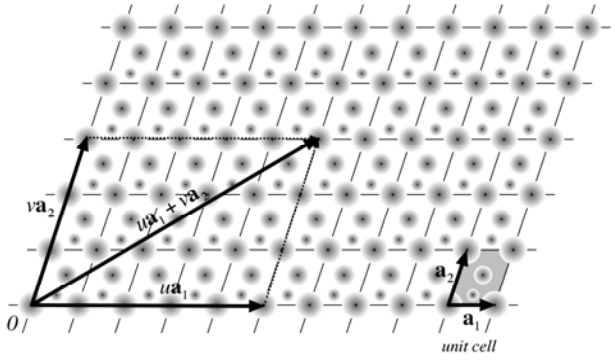
NANO 703-Notes

Chapter 11-Diffraction

Direct lattice

A crystal is a periodic structure in real space. An ideal crystal would have complete translational symmetry through all of space - infinite, that is. So, obviously, there are no ideal crystals, because they all have surfaces. Anyway, a crystal can be subdivided into identical unit cells. All unit cells are equivalent; if we see at the corner of any one of them, the neighboring environment should be the same. There is more than one way to select the unit cell. We usually pick one that highlights the symmetry of the crystal, such as cubic or hexagonal.



Lattice vectors

A real-space (direct) lattice vector can be represented as

$$\mathbf{r}_{uvw} = u\mathbf{a}_1 + v\mathbf{a}_2 + w\mathbf{a}_3$$

where (u,v,w) are integers and $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ are the direct-lattice basis vectors. A reciprocal-space lattice vector can be represented as

$$\mathbf{g}_{hk\ell} = h\mathbf{b}_1 + k\mathbf{b}_2 + \ell\mathbf{b}_3$$

where (h,k,ℓ) are integers and $\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$ are the reciprocal-lattice basis vectors.

Scalar and vector products

There are two ways of "multiplying" vectors. Say we wave two vectors, expressed in Cartesian coordinates:

$$\mathbf{r}_1 = x_1\hat{\mathbf{x}} + y_1\hat{\mathbf{y}} + z_1\hat{\mathbf{z}}$$
$$\mathbf{r}_2 = x_2\hat{\mathbf{x}} + y_2\hat{\mathbf{y}} + z_2\hat{\mathbf{z}}$$

where

$$\hat{\mathbf{x}}\cdot\hat{\mathbf{x}} = 1,\ \hat{\mathbf{x}}\cdot\hat{\mathbf{y}} = 0,\ \hat{\mathbf{x}}\cdot\hat{\mathbf{z}} = 0$$
$$\hat{\mathbf{y}}\cdot\hat{\mathbf{x}} = 0,\ \hat{\mathbf{y}}\cdot\hat{\mathbf{y}} = 1,\ \hat{\mathbf{y}}\cdot\hat{\mathbf{z}} = 0$$
$$\hat{\mathbf{z}}\cdot\hat{\mathbf{x}} = 0,\ \hat{\mathbf{z}}\cdot\hat{\mathbf{y}} = 0,\ \hat{\mathbf{z}}\cdot\hat{\mathbf{z}} = 1$$

The first type of multiplication gives the scalar (dot) product:

$$\mathbf{r}_1\cdot\mathbf{r}_2 = x_1x_2 + y_1y_2 + z_1z_2$$

The second type is the vector (cross) product:

$$\mathbf{r}_1 \times \mathbf{r}_2 = \begin{vmatrix} \hat{\mathbf{x}} & \hat{\mathbf{y}} & \hat{\mathbf{z}} \\ x_1 & y_1 & z_1 \\ x_2 & y_2 & z_2 \end{vmatrix} = (y_1 z_2 - z_1 y_2)\hat{\mathbf{x}} - (x_1 z_2 - z_1 x_2)\hat{\mathbf{y}} + (x_1 y_2 - y_1 x_2)\hat{\mathbf{z}}$$

Determining reciprocal lattice basis vectors

We can write the unit-cell volume using dot and cross products:

$$V = |\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)|$$

We usually want to pick right-handed set of basis vectors, such that $\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3) > 0$. In that case, the reciprocal-lattice basis vectors are related to the direct-lattice basis vectors:

$$\mathbf{b}_1 = \frac{\mathbf{a}_2 \times \mathbf{a}_3}{V}\ , \qquad \mathbf{b}_2 = \frac{\mathbf{a}_3 \times \mathbf{a}_1}{V}\ , \quad \mathbf{b}_3 = \frac{\mathbf{a}_1 \times \mathbf{a}_2}{V}$$

These have some useful properties. For example:

$$\mathbf{b}_i \cdot \mathbf{a}_i = 1, \text{ and } \mathbf{b}_i \cdot \mathbf{a}_j = 0,\ (i \neq j)$$

Matrix representation

In matrix form, vectors appear as column matrices:

$$\mathbf{a}_1 = \begin{pmatrix} a_{1x} \\ a_{1y} \\ a_{1z} \end{pmatrix},\ \mathbf{a}_2 = \begin{pmatrix} a_{2x} \\ a_{2y} \\ a_{2z} \end{pmatrix},\ \mathbf{a}_3 = \begin{pmatrix} a_{3x} \\ a_{3y} \\ a_{3z} \end{pmatrix}$$

We can combine this into a direct-lattice basis matrix:

$$\mathbf{A} = \begin{pmatrix} a_{1x} & a_{2x} & a_{3x} \\ a_{1y} & a_{2y} & a_{3y} \\ a_{1z} & a_{2z} & a_{3z} \end{pmatrix}$$

This lets us write any direct-space vector as:

$$\mathbf{r}_{uvw} = \mathbf{A} \cdot \begin{pmatrix} u \\ v \\ w \end{pmatrix}$$

We can do the same thing for the reciprocal-space basis:

$$\mathbf{b}_1 = \begin{pmatrix} b_{1x} \\ b_{1y} \\ b_{1z} \end{pmatrix},\ \mathbf{b}_2 = \begin{pmatrix} b_{2x} \\ b_{2y} \\ b_{2z} \end{pmatrix},\ \mathbf{b}_3 = \begin{pmatrix} b_{3x} \\ b_{3y} \\ b_{3z} \end{pmatrix}$$

Then

$$\mathbf{B} = \begin{pmatrix} b_{1x} & b_{2x} & b_{3x} \\ b_{1y} & b_{2y} & b_{3y} \\ b_{1z} & b_{2z} & b_{3z} \end{pmatrix}$$

and

$$\mathbf{g}_{hkl} = \mathbf{B} \cdot \begin{pmatrix} h \\ k \\ l \end{pmatrix}$$

Notice that

$$\mathbf{A}^T \cdot \mathbf{B} = \begin{pmatrix} \mathbf{a}_1 \cdot \mathbf{b}_1 & \mathbf{a}_1 \cdot \mathbf{b}_2 & \mathbf{a}_1 \cdot \mathbf{b}_3 \\ \mathbf{a}_2 \cdot \mathbf{b}_1 & \mathbf{a}_2 \cdot \mathbf{b}_2 & \mathbf{a}_2 \cdot \mathbf{b}_3 \\ \mathbf{a}_3 \cdot \mathbf{b}_1 & \mathbf{a}_3 \cdot \mathbf{b}_2 & \mathbf{a}_3 \cdot \mathbf{b}_3 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = I$$

where the *T* superscript represents the matrix transpose, and **1** is the identity matrix. From this we can see that **A** and **B** are different versions of the same thing:

$$\mathbf{B} = \left(\mathbf{A}^T\right)^{-1} = \left(\mathbf{A}^{-1}\right)^T$$

This points us toward a computation method to find **B** if we know **A**, and vice versa. For example, **B** is the inverse of the transpose of **A**.

Another property of RLVs

Notice that the dot product of a reciprocal-lattice vector with a direct-lattice vector gives:

$$\mathbf{g}_{hk\ell} \cdot \mathbf{r}_{uvw} = hu + kv + \ell w = n$$

where n is an integer. So we can say that, for any $(hk\ell)$ and (uvw)

$$e^{2\pi i \mathbf{g}_{hk\ell} \cdot \mathbf{r}_{uvw}} = 1$$

No way we come across a so called "lattice sum", which is a sum over many unit cells. The sum gives

$$\sum_{u,v,w} e^{2\pi i \mathbf{g}_{hk\ell} \cdot \mathbf{r}_{uvw}} = \sum_{n=1}^{N} e^{2\pi i \mathbf{g}_{hk\ell} \cdot \mathbf{r}_n} = \sum_{n=1}^{N} (1) = N$$

where N is the number of unit cells. We will use this result later.

Unit-cell specification

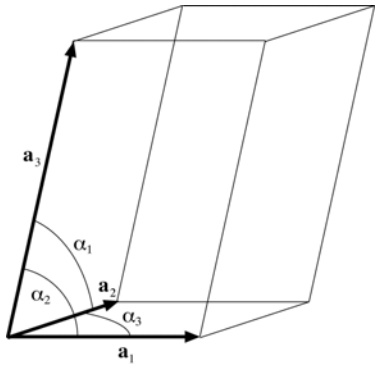
The dimensions of a unit cell can, in general, be specified by six parameters: the lengths of the three direct-lattice basis vectors, called the lattice parameters (or lattice constants), and three angles between the vectors, where

$$a_1 = |\mathbf{a}_1|,\ a_2 = |\mathbf{a}_2|,\ a_3 = |\mathbf{a}_3|$$

and

$$\mathbf{a}_2 \cdot \mathbf{a}_3 = a_2 \cdot a_3 \cdot \cos\alpha_1\ ,\ \mathbf{a}_3 \cdot \mathbf{a}_1 = a_3 \cdot a_1 \cdot \cos\alpha_2\text{, and } \mathbf{a}_1 \cdot \mathbf{a}_2 = a_1 \cdot a_2 \cdot \cos\alpha_3$$

Fewer of these quantities may be needed if we have information on the symmetry of the unit cell. For example, a cubic crystal only requires a single lattice parameter.



Example

As an example, consider an orthorhombic lattice, meaning that $a_1 \neq a_2 \neq a_3 \neq a_1$ and $\alpha_1 = \alpha_2 = \alpha_3 = 90°$. We might as well orient the basis vectors along the Cartesian coordinate axes:

$$\mathbf{a}_1 = a\hat{\mathbf{x}},\ \mathbf{a}_2 = b\hat{\mathbf{y}},\ \mathbf{a}_3 = c\hat{\mathbf{z}}$$

The unit-cell volume is easy to find:

$$V = |\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)| = abc$$

Now find the reciprocal-lattice basis vectors:

$$\mathbf{b}_1 = \frac{\begin{vmatrix} \hat{\mathbf{x}} & \hat{\mathbf{y}} & \hat{\mathbf{z}} \\ 0 & b & 0 \\ 0 & 0 & c \end{vmatrix}}{abc} = \left(\frac{\cancel{b}\cancel{c}\hat{\mathbf{x}}}{a\cancel{b}\cancel{c}}\right) = \left(\frac{1}{a}\right)\hat{\mathbf{x}},\ \mathbf{b}_2 = \frac{\begin{vmatrix} \hat{\mathbf{x}} & \hat{\mathbf{y}} & \hat{\mathbf{z}} \\ 0 & 0 & c \\ a & 0 & 0 \end{vmatrix}}{abc} = \left(\frac{1}{b}\right)\hat{\mathbf{y}},\ \mathbf{b}_3 = \frac{\begin{vmatrix} \hat{\mathbf{x}} & \hat{\mathbf{y}} & \hat{\mathbf{z}} \\ a & 0 & 0 \\ 0 & b & 0 \end{vmatrix}}{abc} = \left(\frac{1}{c}\right)\hat{\mathbf{z}}$$

Notice that the reciprocal lattice is also orthorhombic. The lengths of its basis vectors are the inverses of the lengths of the corresponding direct-lattice basis vectors.

Miller indices

We can define a coordinate system with respect to the direct-lattice basis vectors using

$$\mathbf{a}_1 = a_1\hat{\mathbf{a}}_1,\ \mathbf{a}_2 = a_2\hat{\mathbf{a}}_2, \text{ and } \mathbf{a}_3 = a_3\hat{\mathbf{a}}_3$$

Consider an arbitrary direct-space vector, specified in terms of these basis vectors

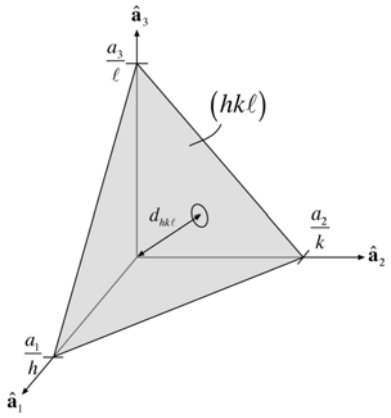
$$\mathbf{r} = x\mathbf{a}_1 + y\mathbf{a}_2 + z\mathbf{a}_3$$

For any real numbers (x, y, z), $\mathbf{r}$ extends from the origin to a point on a plane normal to the RLV $\mathbf{g}_{hk\ell}$ if

$$\mathbf{g}_{hk\ell} \cdot \mathbf{r} = hx + ky + \ell z = A$$

where A is a constant. A plane can generally be expressed in terms of its axis intercepts:

$$\frac{x}{x_i} + \frac{y}{y_i} + \frac{z}{z_i} = 1$$



Now we can find where the plane intersects any of these axes by setting the other coordinates to 0.

$$y = z = 0 \rightarrow x_i = \frac{A}{h},\ z = x = 0 \rightarrow y_i = \frac{A}{k}, \text{ and } x = y = 0 \rightarrow z_i = \frac{A}{\ell}$$

Let's consider a plane passing through lattice points at $(p,0,0)$, $(0,q,0)$, and $(0,0,r)$, where p, q, and r are integers:

$$\frac{x}{p} + \frac{y}{q} + \frac{z}{r} = 1$$

Multiply this by pqr:

$$(qr)x + (pr)y + (pq)z = pqr$$

So there is a plane with $h = qr$, $k = pr$, $\ell = pq$, and $A = pqr$, where h, k, ℓ, and A are integers, that passes through lattice points on the coordinate axes. By allowing A to be any integer, we can generate a set of equally spaced, parallel planes, normal to $\mathbf{g}_{hk\ell}$, with Miller indices $(hk\ell)$.

Interplanar spacing

To find the distance from the origin to any of the $(hk\ell)$ planes, take the dot product of the unit vector normal to the planes with the a vector pointing from the origin to the plane of interest:

$$\frac{\mathbf{g}_{hk\ell}}{|\mathbf{g}_{hk\ell}|} \cdot \mathbf{r} = \frac{hx + ky + \ell z}{|\mathbf{g}_{hk\ell}|} = \frac{A}{|\mathbf{g}_{hk\ell}|}$$

For the $(hk\ell)$ planes, A is any integer. The distance between adjacent planes, say from $A = 0$ to $A = 1$, is the lattice spacing:

$$d_{hk\ell} = \frac{1}{|\mathbf{g}_{hk\ell}|}$$

So we have find that $\mathbf{g}_{hk\ell}$ is normal to the $(hk\ell)$ planes and has length $1/d_{hk\ell}$. We also sometimes specify the direction of $\mathbf{g}_{hk\ell}$ by the Miller indices $(hk\ell)$ of the associated planes.

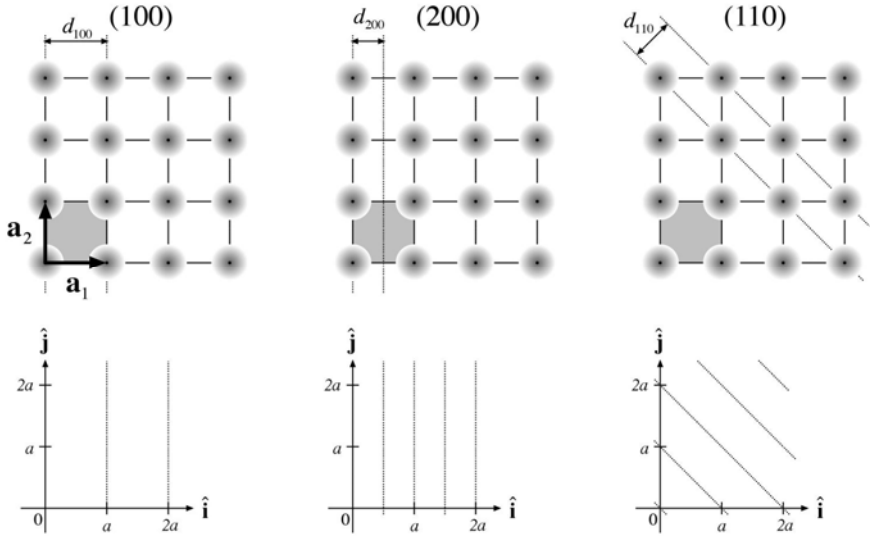
Notation for planes, directions, and reflections

For the purposes of clarity and brevity, notations have been adopted to specify what is being referred to by a particular set of indices, as follows:

Direct Lattice	Reciprocal Lattice	Notation
vector, direction, or point	plane	$[uvw]$
family of vectors or directions	family of planes	$\langle uvw \rangle$
plane	vector, direction or point	$(hk\ell)$
family of planes	family of vectors or directions	$\{hk\ell\}$
diffracting plane	reflection	$hk\ell$

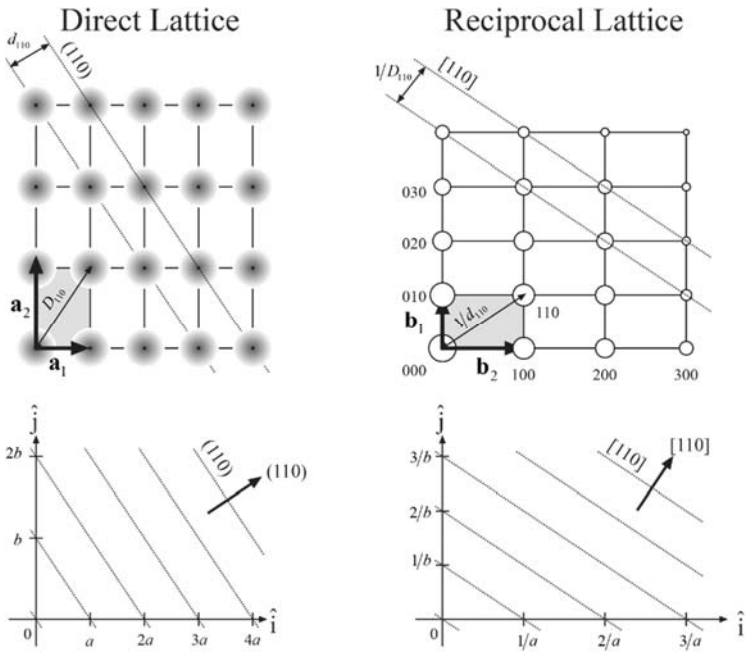
Visualizing direct-lattice planes: Cubic

The planes are abstractions, but the orientation and spacing are not. We can pick any point as the origin, and we usually want the planes to intersect the origin. For a cubic crystal, with lattice parameter a, the (100) planes have spacing a. The (200) planes have the same orientation, but a spacing of only $a/2$. The (110) planes are rotated by 45° and have spacing $a/\sqrt{2}$. For cubic, any direction specified by its the direct-lattice indices, such as $[uvw]$, is the same as that specified by its reciprocal-lattice indices $(hk\ell)$, whenever $h = u$, $k = v$, $\ell = w$.



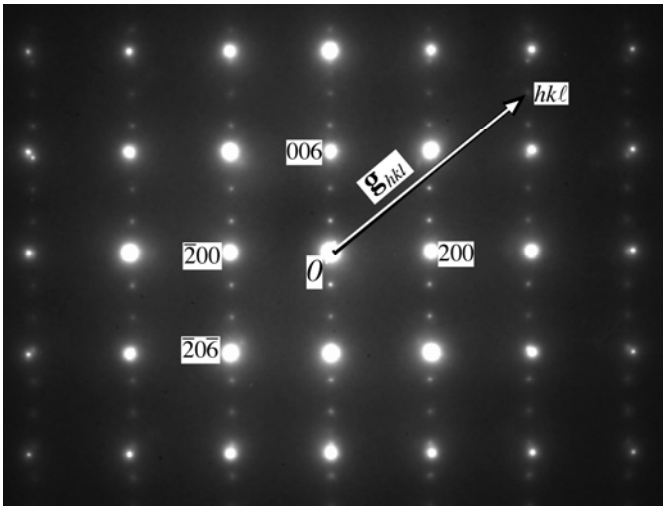
Direct and reciprocal lattices: Non-cubic

The Miller indices $(hk\ell)$ refer to planes in the direct lattice. But there are also planes in the reciprocal lattice, which are described by the indices $[uvw]$. In general, direct- and reciprocal-lattice directions with same indices are not parallel to one another. We saw that the $(hk\ell)$ planes in the direct lattice are perpendicular to the reciprocal-lattice vector $\mathbf{g}_{hk\ell}$, which can also be represented as $(hk\ell)$. Similarly, the $[uvw]$ planes in the reciprocal lattice are perpendicular to the direct-lattice vector $\mathbf{r}_{uvw}$, also represented as $[uvw]$. The distance from (000) (the reciprocal-space origin) to the reciprocal space point $(hk\ell)$ is $1/d_{hk\ell}$, where $d_{hk\ell}$ is the interplanar spacing in direct space. But the distance from $[000]$ (the direct-space origin) to the point $[uvw]$ in direct space is D_{uvw}, where $1/D_{uvw}$ is the interlayer spacing spacing of the perpendicular reciprocal-space planes. Confusing?



Reciprocal lattice vectors and diffraction

Diffraction spots, also called reflections, are indicated by their corresponding lattice planes $hk\ell$ (no parentheses). The vector $\mathbf{g}_{hk\ell}$ points from *0* to the reflection $hk\ell$ (if there is one).



An important lesson here is how to say an expression such as the one that follows:

$(3\ \bar{2}\ 4)$

This means the same as $(3,-2,4)$, but is more compact. The "-" sign above the 2 is equivalent to a "-" sign in front of the 2, as in -2, which is said "negative two", or in this case "three negative two four". But when we see $\bar{2}$, we say "bar two", as in "three bar two four". We do NOT say "two bar", as in "three two bar four", because that would imply $(3\ 2\ \bar{4})$, or $(3,2,-4)$. Whenever we might have said"negative", we can just say "bar".

Bragg condition

The Bragg condition implies that the scattered and incident wave vector differ by an RLV, i.e.:

$$\vec{\mathbf{k}}' = \vec{\mathbf{k}} + \vec{\mathbf{g}}$$

The scattering is elastic, so

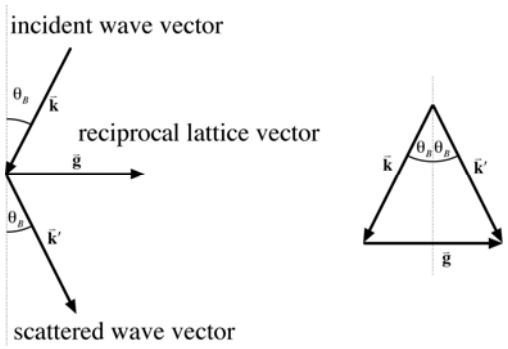
$$k = |\vec{\mathbf{k}}| = |\vec{\mathbf{k}}'| = \frac{1}{\lambda}$$

We now know that

$$g = |\vec{\mathbf{g}}| = \frac{1}{d}$$

Bragg's law must be hidden in there somewhere. Let's square the wave vectors:

$$k^2 = \left(\vec{\mathbf{k}} + \vec{\mathbf{g}}\right)^2 = k^2 + g^2 + 2\vec{\mathbf{k}} \cdot \vec{\mathbf{g}}$$



From the construction, we see that

$$\vec{\mathbf{k}} \cdot \vec{\mathbf{g}} = -k \cdot g \cdot \sin\theta_B$$

So

$$g = 2 \cdot k \cdot \sin\theta_B$$

Yes, this is Bragg's law:

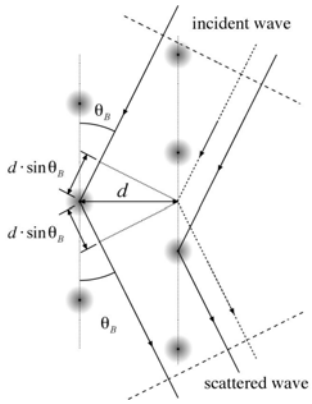
$$2 \cdot d \cdot \sin\theta_B = \lambda$$

In vector form, it can be considered a statement about momentum. The impulse (change in momentum) imparted to the electron in the scattering event is

$$\Delta\vec{\mathbf{p}} = h\left(\vec{\mathbf{k}}' - \vec{\mathbf{k}}\right) = h\vec{\mathbf{g}}$$

Bragg's law: Observations

Bragg's law only mentions the spacing of the planes, not how they line up parallel to the planes. So crystals subject to stacking defects (such as graphite) that maintain a relatively constant interplanar spacing still show Bragg diffraction for those well-stacked planes. Consider the diagram below:



The constructive interference between the adjacent planes, does not depend on how the atoms are lined up normal to the planes.

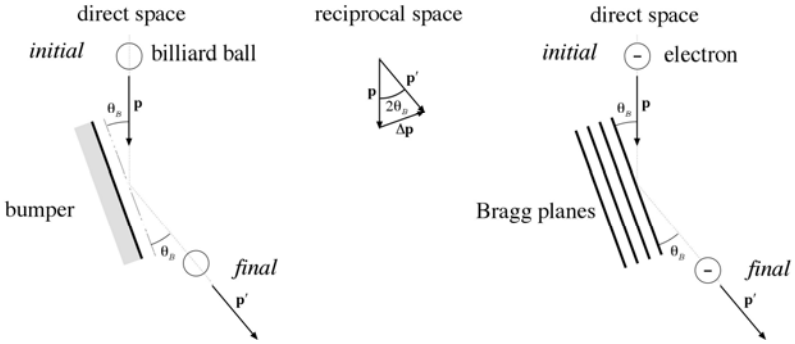
We often see Bragg's law in the form $2d\sin\theta_B = n\lambda$, where *n* is an integer. We don't need the *n*, because we already said $(hk\ell)$ (as in $|\mathbf{g}_{hk\ell}| = 1/d_{hk\ell}$) can be any integers. Dividing by *n*

$$2(d/n)\sin\theta_B = \lambda$$

We can just interpret this to mean $d_{1\cdot(hk\ell)}$, $d_{2\cdot(hk\ell)}$, $d_{3\cdot(hk\ell)}$, etc.

Direct vs. reciprocal space

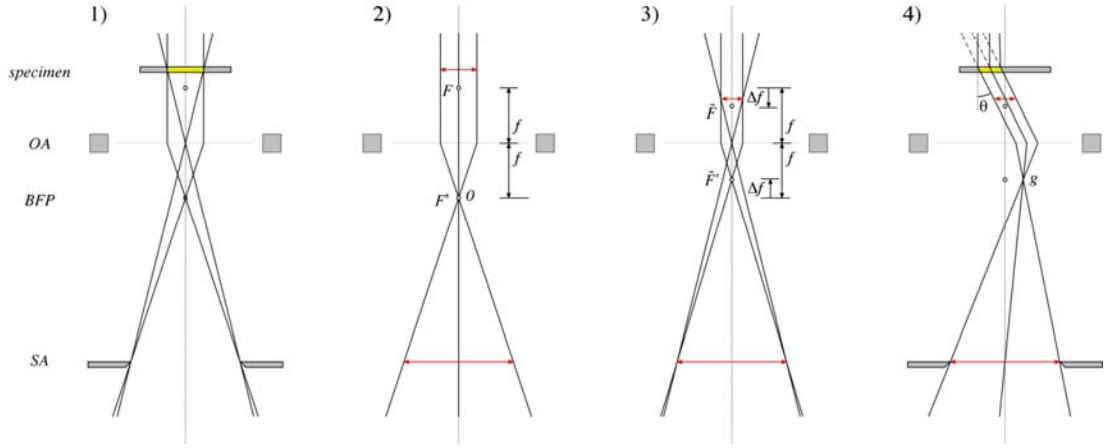
A diagram of scattering in direct space shows trajectories. Bragg diffraction is similar to billiards, in that angles of incidence and reflection are equal, and the lattice planes play the role of bumpers.



But we need the difference of the scattered and incident wave vectors to apply Bragg's law. To find the difference, we have to draw $\mathbf{k}'$ and $\mathbf{k}$, (or $\mathbf{p}'$ and $\mathbf{p}$), with a common origin; the change in wave vector $\Delta\mathbf{k}$ (or momentum $\Delta\mathbf{p}$) closes the triangle.

Selected-area diffraction error

Selected-area diffraction is great… but not perfect. We previously assumed our objective lens has no imperfections. Closer examination shows that, due to spherical aberration of the OL, the area selected is different for different reflections.



Say we select our area in the usual way, with the SA in the first image plane of the OL. Paraxial (undiffracted) beams cross in the OL BFP to form the *0* spot. But diffracted beams make higher angles with respect to the optic axis, so they will be focused more strongly, slightly above the BFP. The object plane corresponding to this shorter focal length is closer to the lens than for the nominal focal length, and the size of the virtual aperture is smaller than the nominal size. When we trace rays diffracted at an angle θ passing through the edges of this virtual aperture, we find that they are sampling not only a smaller region, but one that is laterally shifted from the direct beam. So, the larger the scattering angle for a reflection *g*, the farther off from center is the location of the area selected for that reflection.

Influence of Cs on selected area

We can actually use the SADP shift to measure the C_s of the OL. At high magnification, the shift in the effective object distance is about equal to the shift in focal length: $\Delta p \approx \Delta f$. With spherical aberration, we saw that $\Delta f = C_s\theta^2$. The lateral shift is then $\delta \approx \Delta p \cdot \theta = C_s \cdot \theta^3$.

We can measure the lateral shift between images generated by *0* or *g* by defocusing the intermediate lens in diffraction mode. Now the diffraction spots become disks, and within each disk is an image of the sample area from which it originates. The lateral shift between these images is δ .

If we know the diameter of the virtual SA aperture, we can use that to find the length scale within these images. The scattering angle for the reflection is $\theta = 2\theta_B \approx \lambda/d$. Then use $C_s = \delta/\theta^3$. However, typical estimates give much larger than expected values (e.g., $C_s = 19$ mm), so other contributions appear to dominate the measurement.