BRAGG DIFFRACTION: a more fundamental look with reciprocal lattice vectors

(Here vectors will be displayed in **bold blue**, unit vectors in ***bold violet***, and scalars (and components) in regular black. Complex constants will be displayed in ***bold italic***.) In this section we will use the primitive lattice vectors, the $\mathbf{a}_i$, and we will use the complex form for Fourier Series, $f(\theta) = \Sigma_n \boldsymbol{C_n} e^{in\theta}$.

Instead of assuming planes as we did in the basic look previously, we will drop that assumption in this part and **look at electron densities**.

1. **Basic Idea:** x-rays scatter off electrons that surround atoms; the total amplitude of the scattered x-ray wave will simply be the addition of all the waves scattered off all the electrons.

2. **Review:** any periodic function over a distance, a, (such as electron density in a crystal) can be expressed as a series of sine and cosine functions, or alternatively as series of imaginary exponentials, with $\theta = (2\pi/a)x$ with a being the distance over which the function is periodic.

   a) In 1-D (one dimension), $f(\theta) = \Sigma_n \boldsymbol{C_n} \exp[in\theta] = \Sigma_n \boldsymbol{C_n} \exp[i(n2\pi/a)x] = f(x)$

   or $f(x) = \Sigma_n \boldsymbol{C_n} \exp[iG_n x]$, where $\mathbf{G_n = n(2\pi/a)}$.

   Note: the G_n plays the part of a wavevector, $k_n = 2\pi/\lambda_n$, where $\lambda_n = a/n$

   [recall a and λ both have units of length].

   b) In 3-D, regular x,y,z [conventional cubic] space with a_1 along x, a_2 along y, and a_3 along z:

   $$f(x,y,z) = \Sigma_{n,m,\ell} \boldsymbol{C_{nm\ell}} \exp[i(n2\pi/a_1)x + i(m2\pi/a_2)y + i(\ell 2\pi/a_3)z]$$

   or $$f(x,y,z) = \Sigma_{n,m,\ell} \boldsymbol{C_{nm\ell}} \exp[iG_{nx}x + iG_{my}y + iG_{\ell z}z],$$

   where $G_{nx} = n(2\pi/a_1)$, $G_{my} = m(2\pi/a_2)$, $G_{\ell z} = \ell(2\pi/a_3)$,

   or more simply, $f(r) = \Sigma_G \boldsymbol{C_G} \exp[i\mathbf{G}\bullet\mathbf{r}]$,

   where $\mathbf{G_{nm\ell}} = G_{nx}\boldsymbol{x} + G_{my}\boldsymbol{y} + G_{\ell z}\boldsymbol{z}$ and $\mathbf{r} = x\boldsymbol{x} + y\boldsymbol{y} + z\boldsymbol{z}$.

   Here **G** plays the part of a full 3-D wavevector, **k**.

   c) In 3-D, non-orthogonal space (that is, a_1, a_2, a_3 are not necessarily directed along x,y,z directions), we need to adjust this somewhat: we still have

   $$f(\mathbf{r}) = \Sigma_G \boldsymbol{C_G} \exp[i\mathbf{G}\bullet\mathbf{r}], \quad \text{where} \quad \mathbf{G_{nm\ell}} = G_{nx}\boldsymbol{x} + G_{my}\boldsymbol{y} + G_{\ell z}\boldsymbol{z}.$$

   but we need to satisfy the repeating condition:

   $$f(\mathbf{r}) = f(\mathbf{r}+\mathbf{T}) \quad \text{where} \quad \mathbf{T} = u_1\mathbf{a_1} + u_2\mathbf{a_2} + u_3\mathbf{a_3}$$

where u_1, u_2, and u_3 are integers and the $\mathbf{a_1}$, $\mathbf{a_2}$, and $\mathbf{a_3}$ are the primitive lattice vectors; this then demands that:

$$f(\mathbf{r}) = f(\mathbf{r}+\mathbf{T}) = \Sigma_G \boldsymbol{C_G} \exp[i\mathbf{G}\bullet\mathbf{r}] = \Sigma_G \boldsymbol{C_G} \exp[i\mathbf{G}\bullet(\mathbf{r}+\mathbf{T})$$

$$= \Sigma_G \boldsymbol{C_G} \exp[i\mathbf{G}\bullet\mathbf{r}] \exp[i\mathbf{G}\bullet\mathbf{T}].$$

But the only way that this can be true is for $\mathbf{G}\bullet\mathbf{T} = N2\pi$ where N is an integer
[recall that $\exp(iN2\pi) = \cos(N2\pi) + i\sin(N2\pi) = 1$ if N is an integer]. This can be satisfied if we let:

$$\mathbf{G} = v_1\mathbf{b_1} + v_2\mathbf{b_2} + v_3\mathbf{b_3}$$ such that v_1, v_2 and v_3 are integers,

and $\mathbf{a_1}\bullet\mathbf{b_1} = 2\pi$, $\mathbf{a_2}\bullet\mathbf{b_1} = 0$, $\mathbf{a_3}\bullet\mathbf{b_1} = 0$ (similarly for $\mathbf{b_2}$ and $\mathbf{b_3}$).

This means that $\mathbf{b_1}$ must be perpendicular to both $\mathbf{a_2}$ and $\mathbf{a_3}$; from the vector cross product (used in torque and magnetic field applications) we know that: $(\mathbf{a_2}\times\mathbf{a_3})$ is a vector perpendicular to both $\mathbf{a_2}$ and $\mathbf{a_3}$ as required!

We must also have $\mathbf{a_1}\bullet\mathbf{b_1} = 2\pi$; we can do this by having:

$$\mathbf{b_1} \equiv [2\pi\,\mathbf{a_2}\times\mathbf{a_3}] / [\mathbf{a_1}\bullet(\mathbf{a_2}\times\mathbf{a_3})] .$$ [≡ means definition]

Note that the $\mathbf{b_i}$ vectors have units of inverse distance, the same units as wavevectors.

3. Reciprocal Lattice Vectors

We call the $\mathbf{b_i}$'s **reciprocal lattice vectors**. To see what this means, consider what the $\mathbf{b_i}$'s are: they are a set of **wavevectors**. The **G**'s are made up of integer values of these wavevectors, just like the translation vectors, **T**, are made up of integer values of the primitive lattice vectors, $\mathbf{a_i}$. Hence we can think of the **G**'s as "pointing to points in a wavevector space" similar to the **T**'s as pointing to points in the regular (position) space where these points make up the regular (position) lattice. Since the units of wavevectors [**k**'s] (and hence the $\mathbf{b_i}$'s and **G**'s) are inverse distances, we call the $\mathbf{b_i}$'s and **G**'s **inverse lattice vectors**.

You should be able to do homework problem #8 now.

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4. Deriving the Bragg Law:

We use the periodic electron density, n(**r**), and hence reciprocal lattice vectors since

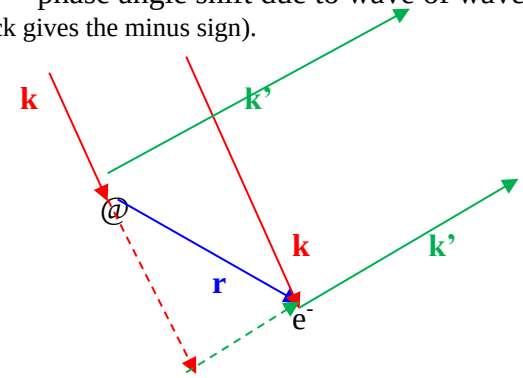
$$n(\mathbf{r}) = n(\mathbf{r}+\mathbf{T}) = \Sigma_G n_G \exp[i\mathbf{G}\bullet\mathbf{r}] = \Sigma_G n_G \exp[i\mathbf{G}\bullet\mathbf{r}]\exp[i\mathbf{G}\bullet\mathbf{T}]$$

in finding the amplitude of scattered x-rays:

Amplitude of scattered x-rays = **A** = addition of all waves scattered from all electrons. Since the exact positions of the electrons are not known, we must use a ***distribution function*** (probability function) of where the electrons are around the atom. We must also take into account the **phase difference** of the scattered waves based on the location of the electron and the wavelength (or wavevector, $k=2\pi/\lambda$) of the x-rays:

$$A = \int n(\mathbf{r}) \exp[i\mathbf{k}\bullet\mathbf{r} - i\mathbf{k}'\bullet\mathbf{r}]\, dV$$

where n(**r**) is the electron distribution function (a Fourier series as mentioned above) as a function of **r**, the location within the basis (**r** is measured from the lattice point), **and the exponential gives the phase relation:** **k**•**r** = phase angle shift due to wave of wavevector **k** moving the distance **r**, (red dotted line in the figure below – recall that the dot product gives the value of k times the value of the component of r in the k direction) and the -**k'**•**r** = phase angle shift due to wave of wavevector **k'** moving **back** the distance **r** (green dotted line - the back gives the minus sign).



If we let $\Delta\mathbf{k} = \mathbf{k}' - \mathbf{k}$, and we use the Fourier expansion for $n(\mathbf{r}) = \Sigma_G n_G \exp[i\mathbf{G}\bullet\mathbf{r}]$:

$$A = \int \Sigma_G n_G \exp(i\mathbf{G}\bullet\mathbf{r}) \exp(-i\,\Delta\mathbf{k}\bullet\mathbf{r})\, dV = \Sigma_G \int n_G \exp(i[\mathbf{G}-\Delta\mathbf{k}]\bullet\mathbf{r}\, dV$$

In general, waves of random phase differences will tend to cancel, so

$$A \approx 0 \text{ if } \mathbf{G} \neq \Delta\mathbf{k}; \qquad A = n_G V \text{ if } \mathbf{G} = \Delta\mathbf{k}\,.$$

Thus the **Bragg condition** for scattered x-rays is $\Delta\mathbf{k} = \mathbf{G}$.

5. Bragg's law for elastic scattering:

If we require the x-rays not to gain or lose any energy on the collision with the electron (elastic scattering - recall the electron can not just gain any energy; it must gain or lose energy only so it can go from one allowed energy level to another):

$E_{x\text{-ray}} = hf = hf'$ (for elastic scattering); this implies that:

$|\mathbf{k}| = |\mathbf{k}'|$ (since $\lambda = \lambda'$ and $k = 2\pi/\lambda$, $k' = 2\pi/\lambda'$) ;

therefore, the condition for scattering x-rays is:

$\Delta\mathbf{k} = \mathbf{G}$, or $\mathbf{k'} - \mathbf{k} = \mathbf{G}$, or $\mathbf{k'} = \mathbf{k} + \mathbf{G}$, so $|\mathbf{k'}| = |\mathbf{k+G}|$, so

$\mathbf{k'} \bullet \mathbf{k'} = (\mathbf{k+G}) \bullet (\mathbf{k+G})$, so $k'^2 = k^2 + 2\mathbf{k}\bullet\mathbf{G} + G^2$,

(but since $|\mathbf{k}| = |\mathbf{k'}|$, $k'^2 = k^2$) , so $-2kG\cos(\theta_{kG}) = G^2$.

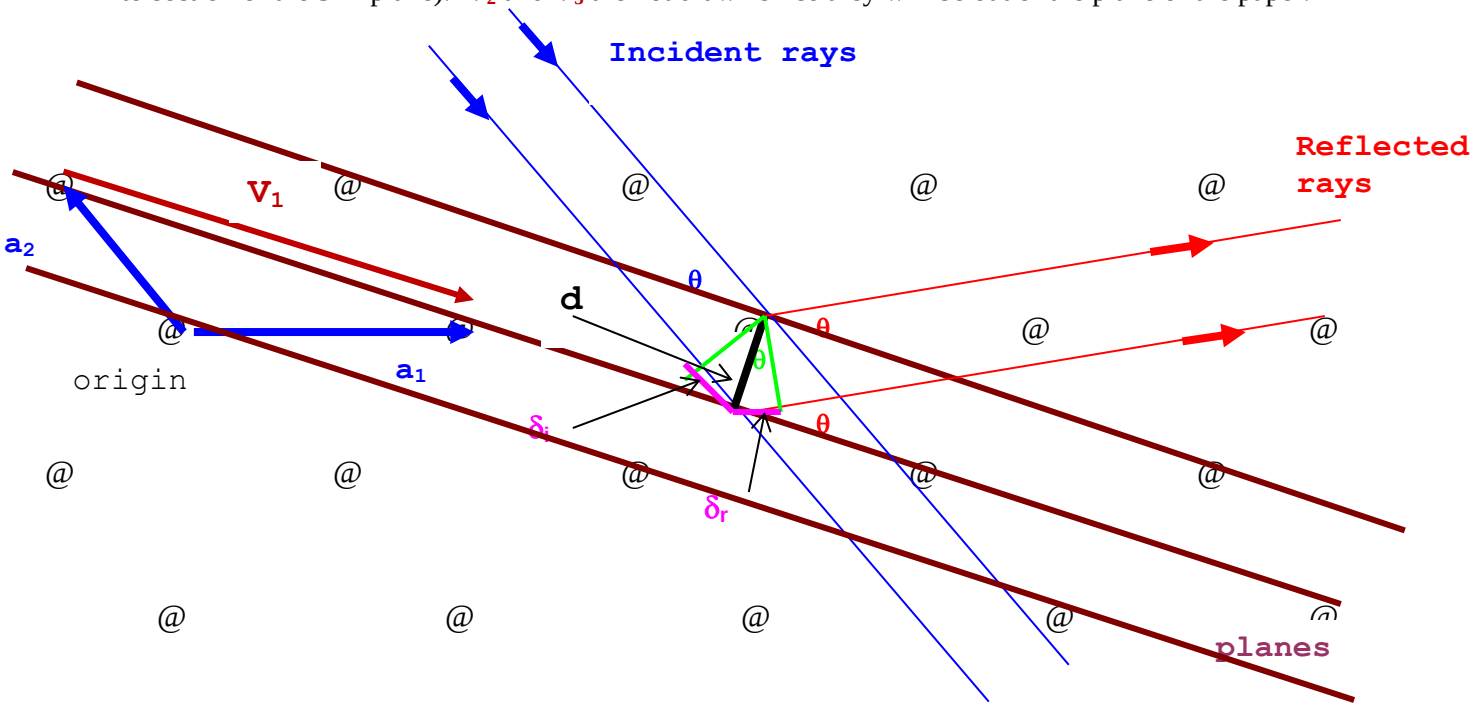
We can also replace G with -G to get rid of the minus sign:

$\mathbf{2k\cos(\theta_{kG}) = G}$, (which is another way of stating **Bragg's law**).

6. Getting the original formula: $n\lambda = 2d\sin(\theta)$

Finally, let's consider where the distance between the planes, d, comes into play in Bragg's law. First consider a plane that intercepts the a_1 axis at ma_1, the a_2 axis at na_2, and the a_3 axis at pa_3 . For this plane to go through lattice points: m, n and p must be integers.

Magnified view of the lattice, with the brown planes being m=1, n=1, and p not specified (since this is just a 2-D intersection of the 3-D plane). $\mathbf{V_2}$ and $\mathbf{V_3}$ are not drawn since they will be out of the plane of the paper.



To get the distance from this plane to the origin (which is in an adjacent plane parallel to this plane), we need to determine the direction that is perpendicular to this plane. To do this, note that the vectors, $\mathbf{V_i}$, are **in the plane**: [note: $n\mathbf{a_2} + \mathbf{V_1} = m\mathbf{a_1}$ so we get:]

$\mathbf{V_1} = m\mathbf{a_1} - n\mathbf{a_2}$, $\mathbf{V_2} = n\mathbf{a_2} - p\mathbf{a_3}$, $\mathbf{V_3} = p\mathbf{a_3} - m\mathbf{a_1}$.

Now let's consider a **G** that we will make perpendicular to this plane that contains the above three vectors. Let's consider the following **G**:

$\mathbf{G} = h\mathbf{b_1} + k\mathbf{b_2} + \ell\mathbf{b_3}$, (h,k,ℓ are integers) .

To make this **G** vector perpendicular to all three of the $\mathbf{V_i}$ vectors, we require:

$\mathbf{G} \bullet \mathbf{V_1} = 0$, or

$$\mathbf{G} \bullet \mathbf{V_1} = (h\mathbf{b_1} + k\mathbf{b_2} + \ell\mathbf{b_3}) \bullet (m\mathbf{a_1} - n\mathbf{a_2}) = 2\pi(mh - nk) = 0$$

recall that $\mathbf{a_i} \bullet \mathbf{b_j} = \{2\pi \text{ if } i=j \text{ or } 0 \text{ if } i\neq j\}$

likewise: $\mathbf{G} \bullet \mathbf{V_2} = 0 = 2\pi(nk - p\ell)$, and $\mathbf{G} \bullet \mathbf{V_3} = 0 = 2\pi(p\ell - mh)$.

To make all three of these relations work out, we can assign h, k and ℓ values as follows: $h = N/m$, $k = N/n$, and $\ell = N/p$, where N is some integer that makes h, k and ℓ all integers. But this procedure for assigning h,k,ℓ integers is just that of assigning the **Miller indices**! Therefore, any **G** vector that has components with values h,k,ℓ will be perpendicular to the $(hk\ell)$ plane.

Now let **s** be any position (distance) vector from the origin to the $(hk\ell)$ plane.

To be definite, let's let $\mathbf{s} = m\mathbf{a_1}$.

Then the perpendicular distance to the $hk\ell$ plane, $d_{hk\ell}$, will be:

$$d_{hk\ell} = \mathbf{s} \bullet \mathbf{G_{hk\ell}} / |\mathbf{G_{hk\ell}}| = 2\pi mh / |\mathbf{G_{hk\ell}}| .$$

But $h = N/m$ so $hm = N$. Therefore $d_{hk\ell} = 2\pi N / |\mathbf{G_{hk\ell}}|$ where N is some integer. Solving this for G: $G = |\mathbf{G_{hk\ell}}| = 2\pi N / d$.

NOTE: FOR A CUBIC LATTICE ($a_1 = a_2 = a_3$ and orthogonal)

$d_{hk\ell} = 2\pi N / G$, but $G = (h^2 + k^2 + \ell^2)^{1/2}(2\pi/a)$, so

$d_{hk\ell} = Na / (h^2 + k^2 + \ell^2)^{1/2}$

Note that as the integers h k ℓ get bigger, $d_{hk\ell}$ gets smaller. You can probably see this if you look at the many different planes drawn in the previous section.

Thus the statement of Bragg's law from part 5 above:

$2k\cos(\theta_{kG}) = G$ can now be written as: $2k\cos(\theta_{kG}) = 2\pi N/d$

recall: k is the wavevector of the x-ray: $k = 2\pi/\lambda$,

N is some integer constant,

d is the perpendicular distance between adjacent planes,

θ_{kG} is the angle between the direction of the x-ray, **k**, and the direction of **G** (which is the direction perpendicular to the plane.)

If we use $k=2\pi/\lambda$ and we use $\cos(\theta_{kG}) = \sin(\theta_{\text{from plane}})$ we can now write Bragg's law as:

$$2(2\pi/\lambda)\sin(\theta_{\text{from plane}}) = 2\pi N/d ,$$

or rearranging:

$$\mathbf{2d\sin(\theta) = N\lambda}$$

(where N is an integer, and θ is the angle the x-ray makes with the surface.)

NOTE: This last form is the original (rough explanation) form of Bragg's law!

Also, recall that the amplitude of the diffracted wave (assuming $\mathbf{\Delta k} = \mathbf{G}$) depends on n_G and usually n_G in a Fourier series gets smaller as G gets bigger (bigger h k ℓ). Note that as h k ℓ gets bigger, the lattice points get further apart and so the density of electrons in that plane get less, so it makes sense that the amplitude would get smaller for bigger G's (bigger h k ℓ).