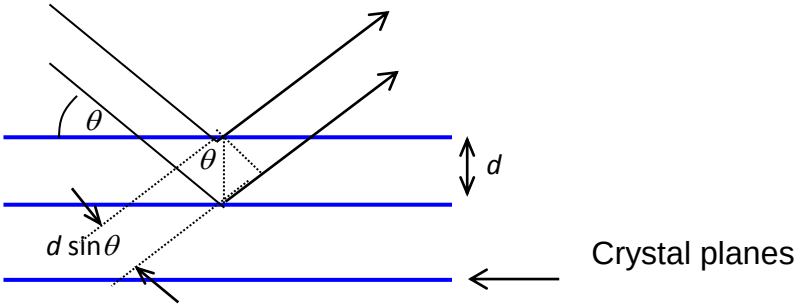
Crystallography: neutron, electron, and X-ray scattering from periodic lattice, scattering of waves by periodic structures, Miller indices, reciprocal space, Ewald construction.

Diffraction:
Specular, elastic scattering angle given by the Bragg law: $2d\sin\theta = n\lambda$



Neutrons: magnetic moment - interacts with magnetic materials or nuclei of non-magnetic materials

$$\varepsilon = \frac{h^2}{2m_n\lambda^2}, \quad m_n = 1.67 \times 10^{-24}\ \text{g} \qquad \lambda = \frac{0.28}{E(\text{eV})^{1/2}}\ (\text{in Å})$$

Electrons: charged - interact strongly with matter - penetrate short distance

$$\varepsilon = \frac{h^2}{2m_e\lambda^2}, \quad m_e = 0.91 \times 10^{-27}\ \text{g} \qquad \lambda = \frac{12}{E(\text{eV})^{1/2}}\ (\text{in Å})$$

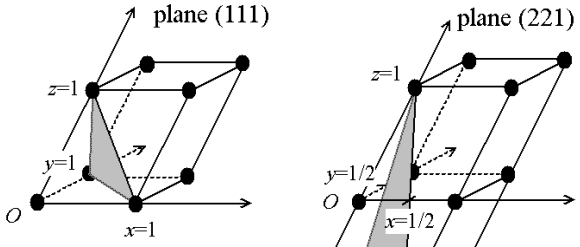
X-rays: nuclei do not scatter X-rays effectively - X-ray photons 'see' only electrons

$\varepsilon = hc/\lambda$, $\lambda = \frac{12.4}{E(\text{keV})}$ (in Å)

Miller indices

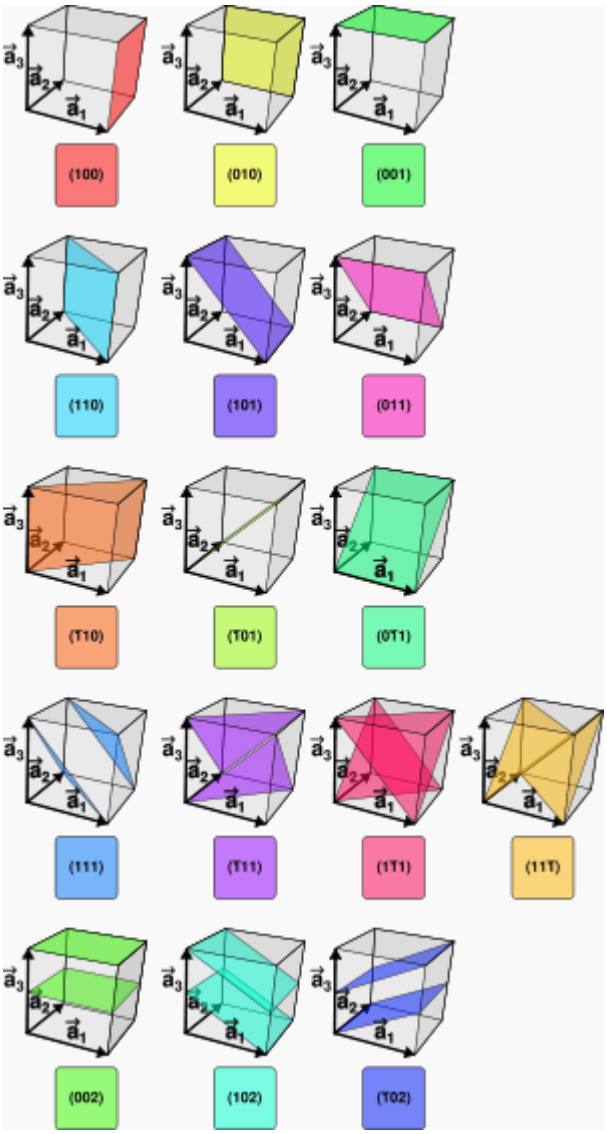
We can see from the above that a set of reflections recorded in an X-ray diffraction experiment can be ascribed to the specific crystal planes. These can be further indexed by three integers *h*, *k*, and *ℓ*, the *Miller indices*, which are usually written as written (hkℓ).

One way to define Miller indices is in a real space where (hkℓ) denotes a plane that intercepts the three points $\mathbf{a}_1/h$, $\mathbf{a}_2/k$, and $\mathbf{a}_3/\ell$, or some multiple thereof. That is, the Miller indices are proportional to the *inverses* of the intercepts of the plane, in the basis of the lattice vectors. If one of the indices is zero, it means that the planes do not intersect that axis.



Source: Wikipedia, author: Christophe Dang Ngoc Chan

Fig. 1. Indexing of crystal planes.



Source: Wikipedia, author DeepKling

Fig.2. Miller indices of various crystal planes in a cubic lattice.

Spacing between planes in cubic lattice:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Reciprocal lattice and Ewald construction

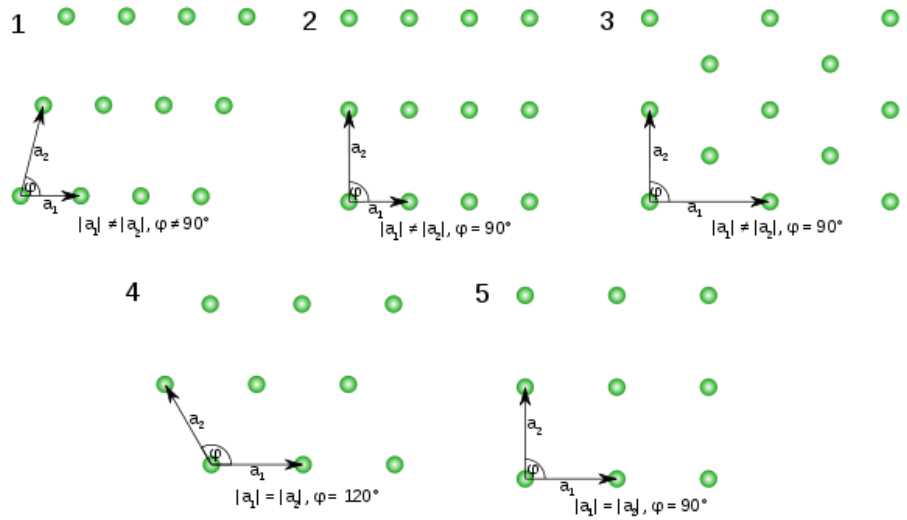
Consider a plane wave described as:

$$e^{i\mathbf{K}\cdot\mathbf{r}} = \cos(\mathbf{K}\cdot\mathbf{r}) + i\sin(\mathbf{K}\cdot\mathbf{r})$$

and a set of points of a Bravais lattice

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$$

where n_i are integers and $\mathbf{a}_i$ are the primitive vectors:



Source: wikipedia, author Prolineserver

Such that plane wave has the same periodicity as a lattice:

$$e^{i\mathbf{K}(\mathbf{r}+\mathbf{R})} = e^{i\mathbf{K}\mathbf{r}}, \text{ or } e^{i\mathbf{K}\mathbf{r}}e^{i\mathbf{K}\mathbf{R}} = e^{i\mathbf{K}\mathbf{r}} \Rightarrow e^{i\mathbf{K}\mathbf{R}} = 1$$

Now, we can introduce a set of points ***K*** that satisfies the above conditions. Such set of points constitutes a reciprocal lattice with primitive reciprocal lattice vectors:

$$\mathbf{b}_1 = 2\pi\frac{\mathbf{a}_2\times\mathbf{a}_3}{\mathbf{a}_1\cdot(\mathbf{a}_2\times\mathbf{a}_3)}$$

$$\mathbf{b}_2 = 2\pi\frac{\mathbf{a}_3\times\mathbf{a}_1}{\mathbf{a}_1\cdot(\mathbf{a}_2\times\mathbf{a}_3)}$$

$$\mathbf{b}_3 = 2\pi\frac{\mathbf{a}_1\times\mathbf{a}_2}{\mathbf{a}_1\cdot(\mathbf{a}_2\times\mathbf{a}_3)}$$

Or in crystallographer's definition simply

$$\mathbf{b}_1 = \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

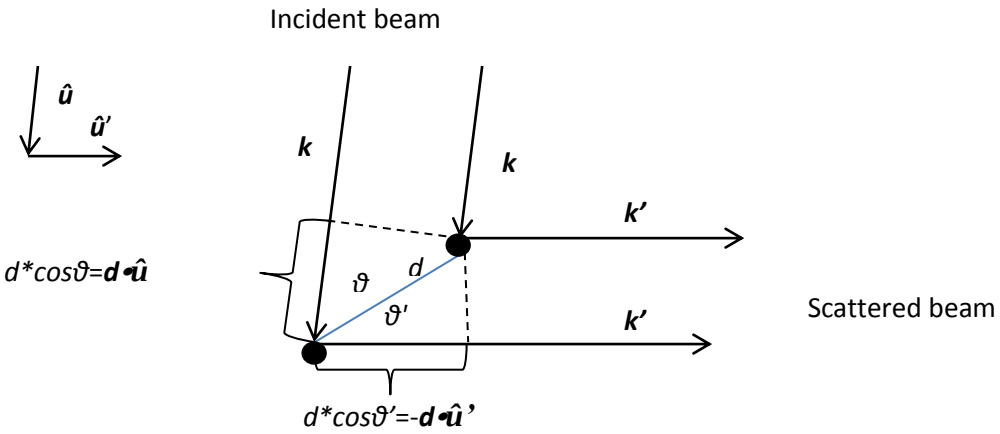
We can observe that by construction each point in the reciprocal lattice corresponds to a set of lattice planes (hkl) in the real space lattice. The direction of the reciprocal lattice vector corresponds to the normal to the real space planes. The magnitude of the reciprocal lattice vector is given in reciprocal length and is equal to the reciprocal of the interplanar spacing of the real space planes.

Reciprocal lattice vector and Laue formulation of the diffraction condition

Similarly to the real space lattice vector $\boldsymbol{T}$ ($=n_1\boldsymbol{a_1}+n_2\boldsymbol{a_2}+n_3\boldsymbol{a_3}$) we define reciprocal lattice vector $\mathbf{g}_{hkl} \equiv \boldsymbol{K} = h\boldsymbol{b_1}+k\boldsymbol{b_2}+l\boldsymbol{b_3}$

The reciprocal vector $\mathbf{g}_{hkl}$ in the reciprocal lattice is always perpendicular to the plane (*hkl*) in the real lattice by construction.

Let's now consider diffraction not from a set of crystal planes, but from periodic scatterers arranged in a Bravais lattice.



And let's find condition for constructive interference for incident ray with $\boldsymbol{k} = 2\pi\boldsymbol{\hat{u}}/\lambda$ and scattered ray with $\boldsymbol{k'} = 2\pi\boldsymbol{\hat{u}'}/\lambda$. We already know that the path difference between two rays must be equal to integral number of wavelength. From the above figure we can see that this path difference is:

$$d^*\cos\vartheta + d^*\cos\vartheta' = \boldsymbol{d}\bullet(\hat{\boldsymbol{u}}-\hat{\boldsymbol{u}}')$$

hence

$$\boldsymbol{d}\bullet(\hat{\boldsymbol{u}}-\hat{\boldsymbol{u}}') = m\,\lambda$$

and multiplying by $2\pi/\lambda$ we get

$$\boldsymbol{d}\bullet(\boldsymbol{k}-\boldsymbol{k}') = 2\pi\, m$$

Now, for an array of scatterers in a Bravais lattice with a lattice vector ***R*** this condition is:

$$\boldsymbol{R}\cdot(\boldsymbol{k}-\boldsymbol{k}') = 2\pi\, m$$

Or equivalently

$$e^{i(\boldsymbol{k}\prime-\boldsymbol{k})\cdot\boldsymbol{R}} = 1$$

But we saw earlier that

$$e^{i\mathbf{K}\mathbf{R}} = e^{i\mathbf{g}\mathbf{R}} = 1$$

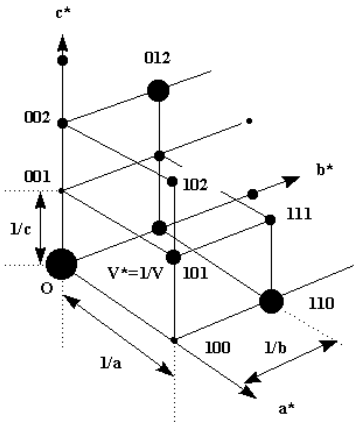
Hence

$$\boldsymbol{g} = \boldsymbol{k}' - \boldsymbol{k}$$

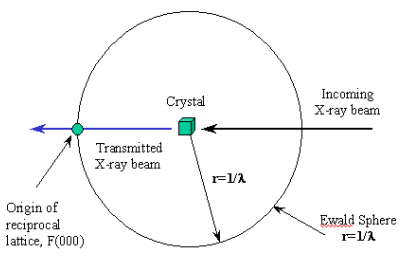
where ***g*** is a reciprocal lattice vector. This is Laue formulation of the diffraction condition and is equivalent to the Bragg condition.

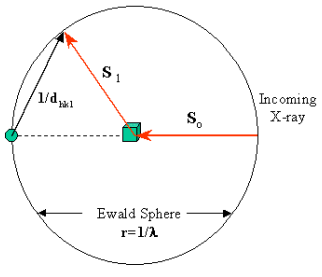
Applications of the reciprocal lattice: Ewald construction

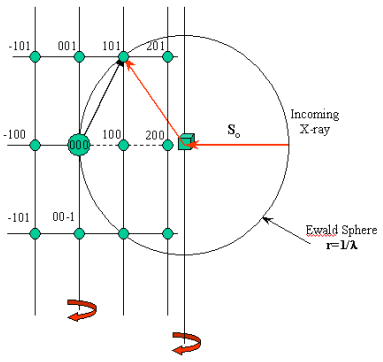
Consider a reciprocal lattice (note that the size of the reciprocal lattice points reflects the intensity of scattering from corresponding real space planes).

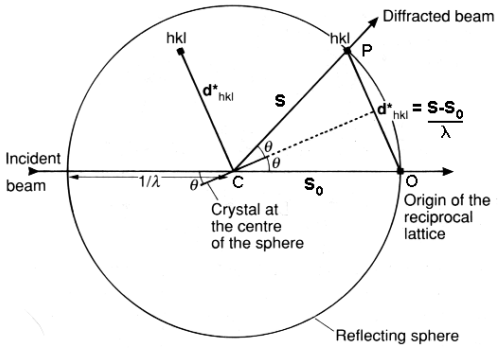


A good visual aid to understanding of occurrence of diffraction spots in case of a single crystal is an *Ewald construction*:









Diffraction will only occur when Bragg conditions are satisfied or which occurs only when a reciprocal lattice point lies on the surface of an Ewald sphere.

Brillouin zone

The first *Brillouin zone* is a uniquely defined primitive cell in reciprocal space. The boundaries of this cell are given by planes related to points on the reciprocal lattice. It is found by the same method as for the Wigner–Seitz cell in the Bravais lattice. The importance of the Brillouin zone stems from the Bloch wave description of waves in a periodic medium, in which it is found that the solutions can be completely characterized by their behavior in a single Brillouin zone.

Taking surfaces at the same distance from one element of the lattice and its neighbours, the volume included is the first Brillouin zone. Another definition is as the set of points in *k*-space that can be reached from the origin without crossing any Bragg plane.

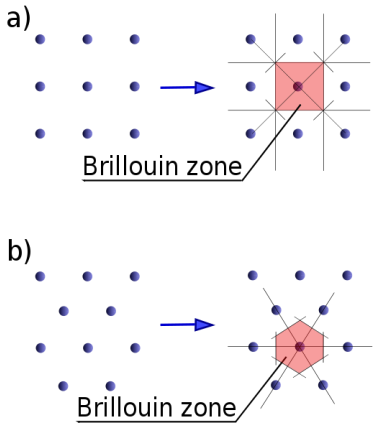


Fig: source: Wikipedia, author Gang65

Relationship between the reciprocal and the real space

Reciprocal lattice of a reciprocal lattice is a real lattice. Reciprocal space (or "k-space") is the space in which the Fourier transform of a spatial function is represented. A Fourier transform takes us from "real space" to reciprocal space or *vice versa*.

$$F(\boldsymbol{k}) = \int_{-\infty}^{\infty} f(\boldsymbol{r}) e^{-i\boldsymbol{k}\boldsymbol{r}} d^3r$$

A reciprocal lattice is a periodic set of points in this space, and contains the ***k*** points that compose the Fourier transform of a periodic spatial lattice. The Brillouin zone is a volume within this space that contains all the unique ***k***-vectors that represent the periodicity of classical or quantum waves allowed in a periodic structure.

Next topic: Electrons in a periodic potential