

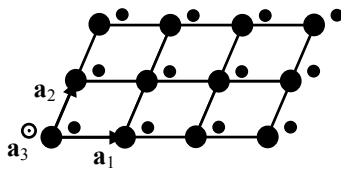
Diffraction from a crystal:

In a crystal, charge density is periodic and can be expanded into a Fourier series:

$$\rho(\mathbf{r}) = \frac{1}{V_c} \sum_{\mathbf{H}} F_{\mathbf{H}} e^{-i\mathbf{H}\cdot\mathbf{r}}, \text{ where } F_{\mathbf{H}} = \sum_j f_j e^{i\mathbf{H}\cdot\mathbf{r}_j} \text{ is the so-called structure factor, } V_c \text{ is}$$

the unit-cell volume. Vector  $\mathbf{H}$  represents a Fourier component, and is called the *reciprocal space vector*. The concept of reciprocal space is so central to diffraction analysis that we probably should spend a few minutes on its basics.

In real space, or direct space, a crystal is made of a periodic lattice (called Bravais lattice) plus a bunch of atoms located at around each lattice site (or atoms within a unit cell).



A unit cell in a Bravais lattice is defined by three unit cell vectors:  $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ , which should be non-coplanar.

$$\text{Unit cell volume } V_c = |\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)|.$$

Any lattice point in direct space can be represented by a lattice vector  $\mathbf{R}_n$ ,

$$\mathbf{R}_n = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3, \text{ where } (n_1, n_2, n_3) \text{ are integers.}$$

Reciprocal space or Fourier space of a crystal is defined by three reciprocal unit cell vectors:  $\mathbf{b}_1 = 2\pi(\mathbf{a}_2 \times \mathbf{a}_3)/V_c$ ,  $\mathbf{b}_2 = 2\pi(\mathbf{a}_3 \times \mathbf{a}_1)/V_c$ ,  $\mathbf{b}_3 = 2\pi(\mathbf{a}_1 \times \mathbf{a}_2)/V_c$ . Any lattice point in reciprocal space can be represented by a reciprocal space vector:

$\mathbf{H} = (hkl) = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$ , with  $(hkl)$  being integers. Reciprocal space is orthogonal to direct space such that  $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$ .

The physical meaning of the reciprocal space vector  $\mathbf{H} = (hkl)$  is the following:

(i) The direction of  $\mathbf{H} = (hkl)$  is perpendicular to the set of atomic planes that intercept the real space lattice ( $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ ) at  $(a_1/h, a_2/k, a_3/l)$ ; and (ii) The magnitude of  $\mathbf{H} = (hkl)$  is  $H = 2\pi/d$ , where  $d$  is the spacing between the lattice planes defined by  $\mathbf{H} = (hkl)$ .

For cubic crystals,  $d = a/\sqrt{h^2 + k^2 + l^2}$ , where  $a$  is the lattice parameter of the cubic unit cell. For other crystal systems, one can find formulas in e.g. Cullity's book. For computer programs, it is often easier to use the notion of metric tensor and dot product to evaluate  $d$ :  $d = 2\pi/\sqrt{\mathbf{H}\cdot\mathbf{H}}$ . Or: one can use the formula for a general triclinic lattice.

Note: two equivalent conventions are used in literature.

(i)  $H = 2\pi/d, k = 2\pi/\lambda \Leftrightarrow$  Plane wave  $e^{-ik\cdot\mathbf{r}}$ , often used by physicists.

(ii)  $H = 1/d, k = 1/\lambda \Leftrightarrow$  Plane wave  $e^{-i2\pi\mathbf{k}\cdot\mathbf{r}}$ , often used by crystallographers.

From what we learned earlier, the scattering amplitude  $S(\mathbf{Q})$  is given by the Fourier transform of the charge density  $\rho(\mathbf{r})$  of the scattering object:

$$S(\mathbf{Q}) = \int_V \rho(\mathbf{r}) e^{i\mathbf{Q}\cdot\mathbf{r}} d\mathbf{r}.$$

For a crystal, any position  $\mathbf{r}$  can be decomposed into  $\mathbf{r} = \mathbf{R}_n + \mathbf{r}'$ , where  $\mathbf{R}_n$  is the lattice vector and  $\mathbf{r}'$  indicates positions inside a unit cell. Thus,

$$\begin{aligned} S(\mathbf{Q}) &= \sum_{n_1} \sum_{n_2} \sum_{n_3} \int_{V_c} \rho(\mathbf{r}') e^{i\mathbf{Q}\cdot(\mathbf{R}_n + \mathbf{r}')} d\mathbf{r}' \\ &= \sum_{n_1} \sum_{n_2} \sum_{n_3} e^{i\mathbf{Q}\cdot\mathbf{R}_n} \int_{V_c} \rho(\mathbf{r}') e^{i\mathbf{Q}\cdot\mathbf{r}'} d\mathbf{r}' \end{aligned}$$

We now write  $\mathbf{Q}$  in reciprocal space:

$$\mathbf{Q} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3, \text{ then } \mathbf{Q}\cdot\mathbf{R}_n = 2\pi(hn_1 + kn_2 + ln_3).$$

Assuming  $N_i$  unit cells exist along  $\mathbf{a}_i$  direction ( $i = 1, 2, 3$ ), then each of the lattice sums gives rise to a  $\sin(Nx)/\sin(x)$  function, and the integral over the unit cell volume yields the structure factor  $F_H$ . Therefore, apart from a phase factor, we have:

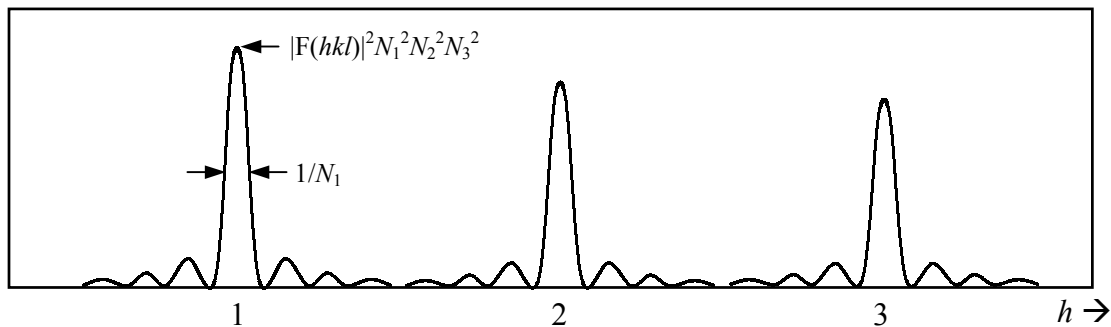
$$S(\mathbf{Q}) = F(\mathbf{Q}) \frac{\sin(\pi h N_1)}{\sin(\pi h)} \frac{\sin(\pi k N_2)}{\sin(\pi k)} \frac{\sin(\pi l N_3)}{\sin(\pi l)},$$

and the scattered intensity:

$$I(\mathbf{Q}) = |F(\mathbf{Q})|^2 \left[ \frac{\sin(\pi h N_1)}{\sin(\pi h)} \right]^2 \left[ \frac{\sin(\pi k N_2)}{\sin(\pi k)} \right]^2 \left[ \frac{\sin(\pi l N_3)}{\sin(\pi l)} \right]^2.$$

This *interference function* shows strong peaks at  $(hkl) = \text{integers}$ , and almost zero everywhere else for any real crystals with  $N_1, N_2, N_3$  greater than say 10. Thus we see that scattered intensity is significant only when the momentum transfer  $\mathbf{Q}$  is equal to a reciprocal space vector  $\mathbf{H}$ :

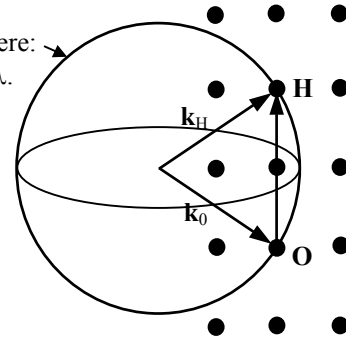
$$I(\mathbf{H}) = |F(hkl)|^2 \left[ \frac{\sin(\pi h N_1)}{\sin(\pi h)} \right]^2 \left[ \frac{\sin(\pi k N_2)}{\sin(\pi k)} \right]^2 \left[ \frac{\sin(\pi l N_3)}{\sin(\pi l)} \right]^2.$$



We can also see that the condition  $\mathbf{Q} = \mathbf{H}$  is equivalent to Bragg's law: since  $Q = 4\pi \sin \theta / \lambda$  and  $H = 2\pi / d$ , we get:  $2d \sin \theta = \lambda$ .

Another useful concept in diffraction analysis is the Ewald sphere construction in reciprocal space (see Figure at right). Any reciprocal nodes that fall on the Ewald sphere give rise to Bragg diffraction peaks.

Ewald sphere:  
radius  $2\pi/\lambda$ .



A diffraction peak can have a finite width, with three types of contributions: size broadening, mosaic spread, and lattice strain. In reciprocal space units, these contributions give rise to:

$\Delta Q = 2\pi / L$ , both transverse and longitudinal, for crystal with average domain size  $L$ ,

$\Delta Q = H \cdot \Delta\theta$ , transverse to  $\mathbf{H}$ , for crystal with mosaic spread  $\Delta\theta$ , and

$\Delta Q = H \cdot \Delta d / d$ , along  $\mathbf{H}$  (longitudinal), for crystal with non-uniform strain  $\Delta d/d$ .

The  $Q$ - and the directional dependence of these contributions can be used to distinguish different possible causes to an observed diffraction peak width.

In an experiment using x-ray diffractometer, a transverse scan is realized by a "rocking" scan or  $q$  scan, while a longitudinal scan is done by rocking the specimen by  $\Delta\theta$  followed by moving the detector by an increment  $2\Delta\theta$ .

