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Some notes on computational crystallography

An overview of crystallography, Crystal systems, Bravais lattices and Miller indices

There are many ways in which radiation (electromagnetic waves, very small particles *etc.*) and matter interact. The purpose of this course is to understand one class of such interactions – elastic scattering (where the scattered radiation neither gains nor loses energy), in the particular case where the wavelength of the radiation is comparable to the spacings between some periodic structures. As we shall see in the next few classes, periodicity plays a key rôle and the first two classes focus on this. In particular, we will review the rules of symmetry that govern crystalline structures.

Crystallography

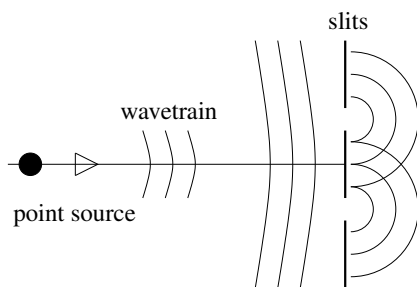
Johannes Kepler recognized in 1611 that the shapes of snow flakes (which are always six-cornered) perhaps reflected the internal arrangement of atoms in the material. He suggested that tiny spheres (of “ice”) pack together to form six-cornered objects. Kepler, incidentally, also suggested that fcc packing is the most efficient way of packing spheres of the same size (inspired, we are told, by looking at the way oranges were stacked in the market). The *proof* that fcc packing is the most efficient was provided only in 1998 (~ 400 y after Kepler). After Kepler, a number of crystallographers, Hooke, Haüy, Barlow, Fedorov *etc.* provided the mathematical basis for crystallography.

Bravais lattices, Crystals systems and Miller indices:

See Hammond.

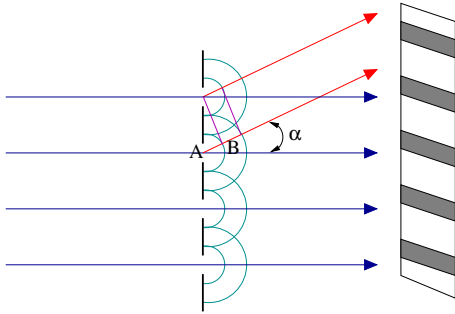
Optical diffraction

Fresnel diffraction



In the Fresnel diffraction experiment, wavetrains from a single point source arrive at two or more slits, through which they pass. The slits act as a secondary light source. As they emerge from the slits, they interfere constructively and destructively, forming dark and light bands.

Fraunhofer diffraction



In Fraunhofer diffraction, a set of parallel rays pass through a number of slits. Constructive and destructive interference occurs as bands on the right hand side. The condition for constructive interference is that the path difference AB, between adjacent slits, should be an integral multiple of the number of wavelengths. If the separation between slits is a , the path difference is:

$$AB = n\lambda = a \sin \alpha$$

If the image is taken at some far-away location, then α is small and $\sin \alpha \sim \alpha$ and

$$\alpha \sim \frac{n\lambda}{a}$$

a reciprocal relationship between the diffraction angle and the (slit) lattice spacings a .

Fourier transforms

The Fourier transform of the function $f(x)$ is defined:

$$F(k) = \int_{-\infty}^{\infty} f(x) e^{-2\pi i k x} dx$$

and its inverse is defined:

$$f(x) = \int_{-\infty}^{\infty} F(k) e^{2\pi i k x} dx$$

For even functions $f(x) = f(-x)$ and only the cosine part of the exponent is retained:

$$F(k) = 2 \int_0^{\infty} f(x) \cos 2\pi k x dx$$

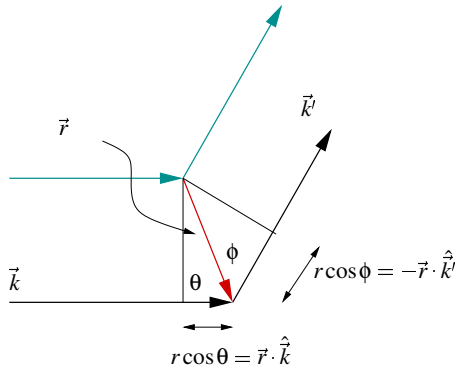
Since the argument of the exponent or the cosine must be dimensionless, the units of k and x are inverses of one-another. So x in \AA means k has the units of \AA^{-1} which is the units of wavenumber. This is a clue that the Fourier transforms of distances (spacings) should be functions of wavenumbers.

A particularly useful Fourier transform is that of the cosine:

$f(x)$	$F(k)$
$\cos(2\pi k_0 x)$	$\frac{1}{2}[\delta(k - k_0) + \delta(k + k_0)]$

A periodic function with wavelength (k_0) is transformed to a single spike, corresponding to that wavelength. Lattices are periodic so one expects that their Fourier transforms will possess information about all the spacings in the lattice.

What is the connection between the scattered/diffracted radiation and the Fourier Transform ?



Consider a “pencil” of radiation being scattered from some point p in an object (black arrows). Let the incident vector be \vec{k} and the scattered vector be \vec{k}' . Now consider the path difference of the scatterer ed vector, with the same pencil of radiation passing through the origin in the object. This is represented by the green arrows. The vector \vec{r} (red) allows the path difference to be calculated as:

$$r \cos \theta + r \cos \phi = \vec{r} \cdot \hat{k} + -\vec{r} \cdot \hat{k}'$$

So the path difference is

$$\vec{r} \cdot (\hat{k} - \hat{k}')$$

Now since the phase difference is the path difference times $2\pi/\lambda$, we have the phase difference:

$$\vec{r} \cdot (\hat{k} - \hat{k}') \times 2\pi/\lambda$$

Let $\vec{q} = \lambda(\hat{k} - \hat{k}')$. Then the phase difference is $2\pi\vec{r} \cdot \vec{q}$. The corresponding wave is then $\exp(2\pi i\vec{r} \cdot \vec{q})$. Now if we integrate over all points in the object, and $f(\vec{r})$ represents the amplitude of the scattering at the point described by \vec{r} , then the total scattering is

$$F(\vec{q}) = \int_{-\infty}^{\infty} f(\vec{r}) e^{(2\pi i\vec{r} \cdot \vec{q})} d\vec{r}$$

Which is nothing but the Fourier transform

The generation of X-rays

Electrons from a glowing filament (usually tungsten or rhenium) are accelerated by applying a DC field (typically of about 30-40 kV). These accelerated electrons are then bombarded against a cooled metal target (Fe, Cu, Mo . . .). The electrons slow down when they enter the metal, so they loose energy. This lost energy is emitted as a continuous radiation called *brehmsstrahlung* radiation, usually in the X-ray region of the electromagnetic spectrum (with energies of the order of kV). In addition to the broad *brehmsstrahlung* radiation, there are the so-called *characteristic X-ray* peaks associated with electronic transitions in the target material. These characteristic X-radiations have a much larger intensity than does the *brehmsstrahlung*. The energies of the characteristic radiation depends on which atomic shell of the target material is being excited by the incident electrons (K, L *etc*), as well as the atomic number of the target. The energy of the characteristic radiation is proportional to the atomic number raised to the fourth power.

In lab X-ray diffraction experiments, characteristic radiation from the K shell of Cu (with a wavelength around 1.5 Å) or from the K shell of Mo (with a wavelength around 0.7 Å) is typically used.

When charged particles are accelerated, they release energy continuously. In a synchrotron source, electrons are typically accelerated around a storage ring through the use of magnetic fields. The accelerated electrons emit X-rays when they are sufficiently energized. This X-radiation covers a broad spectrum of wavelengths and is very useful for a number of scattering experiments for which lab X-rays are not suited.

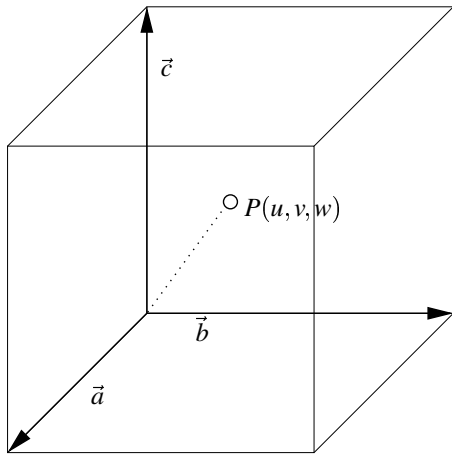
The Laue experiment

In the Laue experiment, the crystal is viewed as a 3D diffraction grating. Vector analysis can be used to determine the path difference in the scattered radiation induced by the crystal lattice. The analysis is similar to our demonstration that the scattering corresponds to a Fourier transform. See the handout.

The Bragg experiment and Bragg's law

Bragg simplified the Laue picture by saying that planes (constituted of atoms) can be assumed to act like mirrors and that the X-rays undergo specular reflection by these mirrors. The path difference between the reflected rays from adjacent mirrors gives rise to constructive and destructive interference. See the handout.

The direct lattice



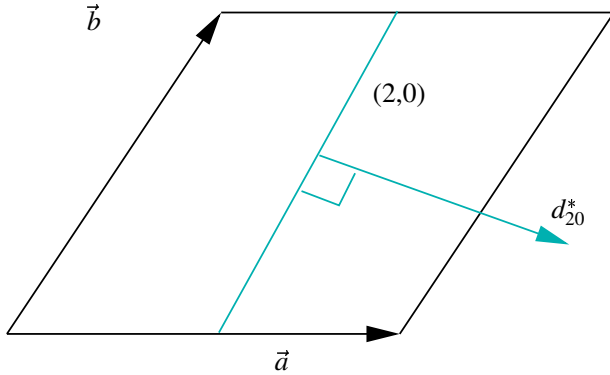
We have so far considered the unit cell with the origin at some corner and the sides described by a , b and c . However, we also recognize that three edges of the unit cell starting from the origin describe the *direct lattice vectors* \vec{a} , \vec{b} and \vec{c} . Then some point $P(u, v, w)$ within the unit cell where (u, v, w) could have fractional coordinates, meaning:

$$\{u, v, w\} \in \{[0, 1], [0, 1], [0, 1]\}$$

To obtain the position of P in real coordinates, we then have

$$P = u\vec{a} + v\vec{b} + w\vec{c}$$

The reciprocal lattice



Consider in 2D, the two vectors \vec{a} and \vec{b} describing a lattice. The Miller plane (or line) $(2,0)$ is indicated as a cyan line. Remember that by definition, the $(2,0)$ line intercepts the a axis at $a/2$ and the b axis at $b/0 = \infty$. Now define a perpendicular vector \vec{d}_{20}^* to the Miller line $(2,0)$ whose length is given by:

$$|\vec{d}_{20}^*| = \frac{K}{d_{20}}$$

Where d_{20} is the perpendicular distance between parallel $(2,0)$ lines and K is some constant. The reason why the modulus of the vector is inversely proportional to the d spacing arises from the way the Miller indices are defined as the inverse of the intercepts. The vector \vec{d}_{20}^* has the units of inverse length and is an example of a vector in the reciprocal lattice.

It is easy to see that if we defined a set of three *reciprocal lattice vectors* \vec{a}^* , \vec{b}^* and \vec{c}^* in 3D, such that:

$$\vec{a}^* = \vec{d}_{100}^* \text{ and } |\vec{a}^*| = \frac{1}{d_{100}}$$

$$\vec{b}^* = \vec{d}_{010}^* \text{ and } |\vec{b}^*| = \frac{1}{d_{010}}$$

$$\vec{c}^* = \vec{d}_{001}^* \text{ and } |\vec{c}^*| = \frac{1}{d_{001}}$$

Then any vector in the reciprocal lattice can be described:

$$\vec{d}_{hkl}^* = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$$

This vector is parallel to the family of (hkl) Miller planes. This description should be compared with:

$$P = u\vec{a} + v\vec{b} + w\vec{c}$$

Therefore, in the reciprocal lattice, the Miller indices serve as components of the corresponding vector.

Some important relations concerning the reciprocal lattice

$$\vec{a}^* \cdot \vec{b} = \vec{a}^* \cdot \vec{c} = \vec{b}^* \cdot \vec{a} = \vec{b}^* \cdot \vec{c} = \vec{c}^* \cdot \vec{a} = \vec{c}^* \cdot \vec{b} = 0$$

and

$$\vec{a}^* \cdot \vec{a} = \vec{b}^* \cdot \vec{b} = \vec{c}^* \cdot \vec{c} = 1$$

The first relation suggests that \vec{a}^* is normal to the plane (b, c) , \vec{b}^* is normal to (a, c) and \vec{c}^* is normal to (a, b) . The modulus and sense of the reciprocal lattice vectors are fixed by the second relation. The relations suggest that we could write:

$$\vec{a}^* = p(\vec{b} \times \vec{c}); \quad \vec{b}^* = p(\vec{c} \times \vec{a}); \quad \vec{c}^* = p(\vec{a} \times \vec{b})$$

Where p is a constant. The value of p is given by taking the dot product of both sides of

$$\vec{a}^* = p(\vec{b} \times \vec{c})$$

by \vec{a} , so that

$$\vec{a}^* \cdot \vec{a} = 1 = p(\vec{b} \times \vec{c} \cdot \vec{a})$$

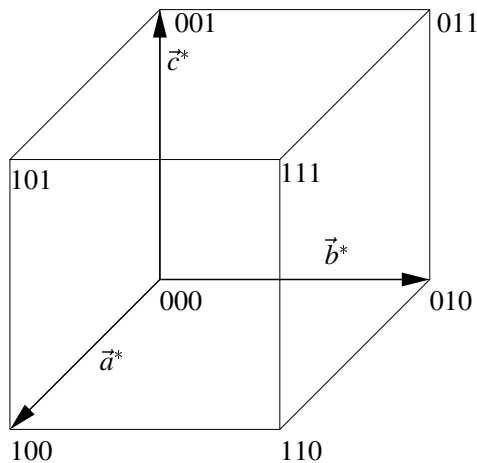
But the scalar triple product is just the volume V

$$V = \vec{b} \times \vec{c} \cdot \vec{a}$$

This tells us that $p = 1/V$ and

$$\vec{a}^* = (\vec{b} \times \vec{c})/V; \quad \vec{b}^* = (\vec{c} \times \vec{a})/V; \quad \vec{c}^* = (\vec{a} \times \vec{b})/V$$

The reciprocal unit cell will have as coordinates at the corners, the sets of Miller planes which are perpendicular to the reciprocal lattice vectors. For a cubic cell, the reciprocal cell:



Distances

Since the length of the vector \vec{d}_{hkl}^* is inversely related to the perpendicular distance between neighboring hkl planes,

$$\vec{d}_{hkl}^* \cdot \vec{d}_{hkl}^* = \frac{1}{d_{hkl}^2} = (h\vec{a}^* + k\vec{b}^* + l\vec{c}^*) \cdot (h\vec{a}^* + k\vec{b}^* + l\vec{c}^*)$$

For orthorhombic crystals, $\vec{a}^* \cdot \vec{b}^* = 0$ etc. and $\vec{a}^* \cdot \vec{a}^* = 1/a^2$ etc. This gives:

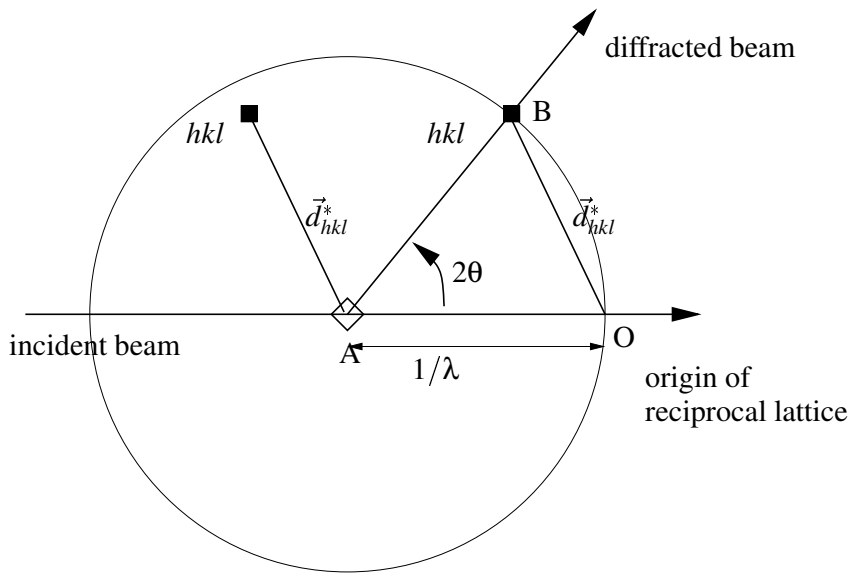
$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

Angles

The angles between normals to the planes described by $(h_1k_1l_1)$ and $(h_2k_2l_2)$ is described by:

$$\cos \rho = \frac{\vec{d}_{h_1k_1l_1}^* \cdot \vec{d}_{h_2k_2l_2}^*}{|\vec{d}_{h_1k_1l_1}^*| |\vec{d}_{h_2k_2l_2}^*|}$$

The Ewald construction



We draw a sphere of radius $1/\lambda$ around the crystal at A. If the incident x-ray beam is diffracted through the point B (the Bragg condition is satisfied for some hkl plane) then we consider the reciprocal lattice vector \vec{d}_{hkl}^* , starting at the origin O, and extending to B. By trigonometry, we have:

$$OB/2 = (1/\lambda) \sin \theta = (1/2) |\vec{d}_{hkl}^*| = 1/(2d_{hkl})$$

or

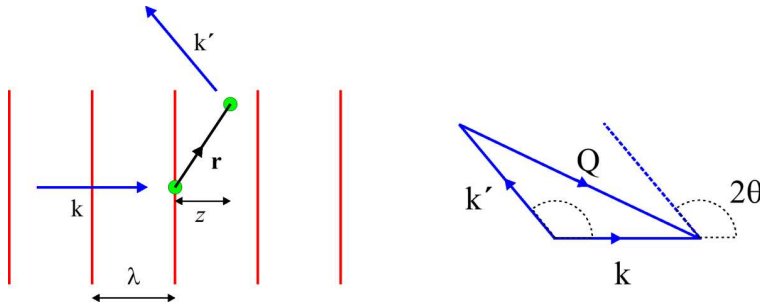
$$\lambda = 2d_{hkl} \sin \theta$$

Therefore the Bragg condition is fulfilled if one of the reciprocal lattice points falls on the Ewald sphere.

The atomic form factor

This discussion closely follows: *Elements of Modern X-ray Physics*, by Jens Als-Nielsen and Des Morrow, John Wiley & Sons, Ltd (2001), and makes use of figures from their book <http://ntserv.fys.ku.dk/XBook/>.

Consider the scattering of x-rays from two electrons, one at the origin and the other separated by a distance \vec{r} . Let an incident x-ray of wavevector \vec{k} be scattered elastically to some \vec{k}' after it leaves the second electron.



The scattering wavevector \vec{q} is defined as:

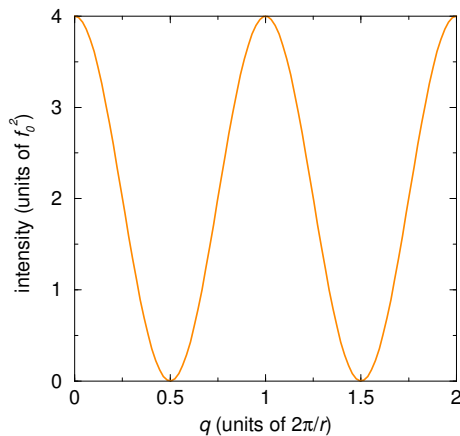
$$|\vec{q}| = \left(\frac{4\pi}{\lambda}\right) \sin \theta = \frac{2\pi}{d}$$

The diffraction condition is provided by the phase difference $\phi = (\vec{k} - \vec{k}') \cdot \vec{r} = \vec{q} \cdot \vec{r}$
 The scattering amplitude is given by:

$$A(\vec{q}) = f_0 + f_0 e^{i\vec{q} \cdot \vec{r}} = f_0(1 + e^{i\vec{q} \cdot \vec{r}})$$

The scattered intensity is the square of the scattering amplitude:

$$I(\vec{q}) = A(\vec{q})A(\vec{q})^* = 2f_0^2[1 + \cos(\vec{q} \cdot \vec{r})]$$



Scattering from 2 electrons separated by \vec{r} when \vec{q} is in the same direction as \vec{r} .

What is f_0 ? It reflects the ability of the electron to scatter. In the case of atoms, f_0 is replaced by f , the atomic scattering factor:

$$\text{atomic scattering factor } f = \frac{\text{amplitude of scattering by atom}}{\text{amplitude of scattering by a single electron}}$$

Consider an atom has with a spherically symmetric distribution of electrons This distribution is represented by some $\rho(\vec{r})$. The scattering from the entire atom can be written as an integral over all the space within which the electrons are enclosed.

$$f(\vec{q}) = \int \rho(\vec{r}) e^{i\vec{q}\cdot\vec{r}} d\vec{r}$$

where $e^{i\vec{q}\cdot\vec{r}}$ is the usual phase factor. The limiting conditions are $\vec{q} \rightarrow 0$ when $f = Z$ (where Z is the atomic number), and $\vec{q} \rightarrow \infty$ when $f = 0$. At $\vec{q} = 0$, all the scattered radiation is in phase. When \vec{q} start to become large, the phase differences between the scattering will increase and destructive interference will tend to drive the scattering to 0.

The form factors of “floppy” atoms and ions tend to die out faster than the form factors of “compact” atoms.

Tabulations of the form factor

The calculated¹ form factors for the different elements and their important ions can be found tabulated using nine terms. For example, for Si:

a_1	b_1	a_2	b_2	a_3	b_3	a_4	b_4	c
6.2915	2.4386	3.0353	32.333	1.9891	0.6785	1.5410	81.6937	1.1407

The following function makes use of these 9 constants to evaluate $f(s)$ where $s = q/4\pi = (\sin \theta)/\lambda$:

$$f(s) = \sum_{j=1}^4 a_j e^{-b_j s^2} + c$$

Go to <http://www-structure.llnl.gov/Xray/comp/scatfac.htm> to make plots of $f(s)$ for different elements.

Form factors for neutrons

When nuclei (which are very very small) scatter neutrons with wavelengths of the order of 1 Å, s is effectively 0 and the scattering (the so-called scattering length) remains constant throughout the scattering diagram.

The Debye formula

Based on an extension of the two-electron scattering problem (see Als-Nielsen) one can arrive at the very general Debye formula for scattering of X-rays by molecules, crystals *etc.* For N atoms, each with its form factor f_j , the scattering intensity is given by:

¹Such calculations by D. T. Cromer form some of the most cited papers of all time

$$\begin{aligned}
\left\langle \left| \sum_{j=1}^N f_j e^{i\vec{q}\cdot\vec{r}_j} \right|^2 \right\rangle_{\text{orient. av.}} &= |f_1|^2 + |f_2|^2 + \dots + |f_N|^2 \\
&+ 2f_1f_2 \frac{\sin(qr_{12})}{qr_{12}} + \dots + 2f_1f_N \frac{\sin(qr_{1N})}{qr_{1N}} + \dots \\
&+ 2f_2f_3 \frac{\sin(qr_{23})}{qr_{23}} + \dots + 2f_2f_N \frac{\sin(qr_{2N})}{qr_{2N}} + \dots \\
&+ 2f_{N-1}f_1 \frac{\sin(qr_{N-1,1})}{qr_{N-1,1}} + \dots + 2f_{N-1}f_N \frac{\sin(qr_{N-1,N})}{qr_{N-1,N}}
\end{aligned}$$

The different r_{ij} represent the distances between atom i and atom j . So given a system where all the atom positions are known, the scattering can be calculated. This applies for glasses, crystals, nanoparticles ...

The structure factor

See Hammond and the handout.

Friedel's law

See Hammond and the handout.

The crystallographic phase problem

Since the measured intensities are the square of the structure factor, we obtain from the intensities, information about scattering amplitudes, but not phases. This is called the phase problem, and while there is no solution, there are many ways around it.

Structure factors

The structure factor for a system with many atoms, each with its own form factor f_j and sitting within the unit cell at a site with the crystallographic coordinates (u_j, v_j, w_j) is described by:

$$F_{hkl} = \sum_{j=1}^N f_j \exp[2\pi i(hu_j + kv_j + lw_j)]$$

The square of the structure factor is an indication of the intensity of any spot/peak/intensity in the diffraction pattern corresponding to the Bragg conditions being satisfied for the particular hkl . There are other contributors to the intensity, such as the Lorentz-polarization factors and the Debye-Waller factor that we will discuss at a later stage.

Some applications:

CsCl

The CsCl structure is simple cubic ($Pm\bar{3}m$) with the Cs atom at the corners of a cube at $(0,0,0)$ and the Cl atom at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The structure factor for any hkl reflection is:

$$F_{hkl} = f_{\text{Cs}} \exp[2\pi i(h0 + k0 + l0)] + f_{\text{Cl}} \exp[2\pi i(h\frac{1}{2} + k\frac{1}{2} + l\frac{1}{2})]$$

which simplifies to

$$F_{hkl} = f_{\text{Cs}} + f_{\text{Cl}} \exp[\pi i(h + k + l)]$$

When

$(h + k + l)$ is even, $\exp[\pi i(h + k + l)] = 1$ and when $(h + k + l)$ is odd, $\exp[\pi i(h + k + l)] = -1$

This means, for CsCl:

$$F_{hkl} = \begin{cases} f_{\text{Cs}} + f_{\text{Cl}}, & \text{if } (h + k + l) \text{ is even;} \\ f_{\text{Cs}} - f_{\text{Cl}}, & \text{if } (h + k + l) \text{ is odd} \end{cases}$$

For an hcp metal

The atoms are at $(0,0,0)$ and $(\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$, and both atoms have a form factor f :

$$F_{hkl} = f + f \exp[2\pi i(h\frac{1}{3} + k\frac{2}{3} + l\frac{1}{2})]$$

We consider specific cases:

$$F_{001} = f + f \exp[\pi i] = f - f = 0$$

$$F_{002} = f + f \exp[2\pi i] = f + f = 2f$$

$$F_{100} = f + f \exp[\frac{2\pi i}{3}] = f\frac{1}{2} + if\frac{\sqrt{3}}{2}$$

$$F_{101} = f + f \exp[2\pi i(\frac{1}{3} + \frac{1}{2})] = f\frac{3}{2} - if\frac{\sqrt{3}}{2}$$

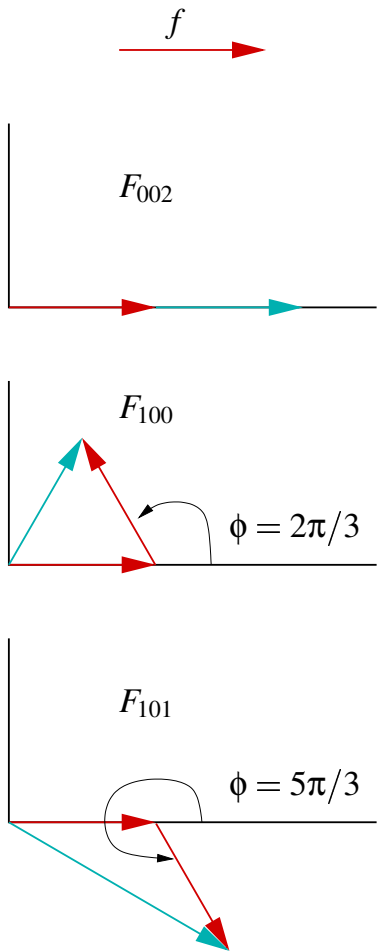
The corresponding intensities are obtained from

$$I_{hkl} = F_{hkl} \cdot F_{hkl}^*$$

Thus

$$I_{001} = 0; I_{002} = 4f^2, I_{100} = f^2, I_{101} = 3f^2$$

The Argand diagram can be used to graphically represent F_{hkl} :



Diffraction from a centrosymmetric crystal

In a centrosymmetric crystal, (u, v, w) and $(-u, -v, -w)$ represent the same point. Note that negative numbers are also written with overlines: $-u = \bar{u}$. In other words, for any atom with form factor f at the position (u, v, w) , there is an identical atom at $(\bar{u}, \bar{v}, \bar{w})$. Together, the structure factor due to these is:

$$\begin{aligned}
 F_{hkl} &= f \exp[2\pi i(hu + kv + lw)] + f \exp[2\pi i(h\bar{u} + k\bar{v} + l\bar{w})] \\
 &= f \exp[2\pi i(hu + kv + lw)] + f \exp[-2\pi i(hu + kv + lw)]
 \end{aligned}$$

Now $\exp(i\phi) + \exp(-i\phi) = \cos \phi + i \sin \phi + \cos \phi - i \sin \phi = 2 \cos \phi$

This means that for a centrosymmetric crystal,

$$F_{hkl} = 2f \cos[2\pi(hu + kv + lw)]$$

Friedel's Law

Friedel's law states that even if a crystal does not possess a center of symmetry, its diffraction pattern does.

$$\begin{aligned}
I_{hkl} &= F_{hkl} \cdot F_{hkl}^* = f \exp[2\pi i(hu + kv + lw)] \times f \exp[-2\pi i(hu + kv + lw)] \\
&= f \exp[2\pi i(hu + kv + lw)] \times f \exp[2\pi i(\bar{h}u + \bar{k}v + \bar{l}w)]
\end{aligned}$$

By the same token,

$$\begin{aligned}
I_{\bar{h}\bar{k}\bar{l}} &= F_{\bar{h}\bar{k}\bar{l}} \cdot F_{\bar{h}\bar{k}\bar{l}}^* = f \exp[2\pi i(\bar{h}u + \bar{k}v + \bar{l}w)] \times f \exp[-2\pi i(\bar{h}u + \bar{k}v + \bar{l}w)] \\
&= f \exp[2\pi i(\bar{h}u + \bar{k}v + \bar{l}w)] \times f \exp[2\pi i(hu + kv + lw)]
\end{aligned}$$

In other words:

$$F_{hkl} = F_{\bar{h}\bar{k}\bar{l}}^* \text{ and } F_{\bar{h}\bar{k}\bar{l}} = F_{hkl}^*$$

and $I_{hkl} = I_{\bar{h}\bar{k}\bar{l}}$.

Friedel's law is violated in the case when diffraction is *anomalous*.

The phase problem

Simply stated, what is measured in an experiment is I_{hkl} , but what is required is F_{hkl} . There is no information of phase in I_{hkl} .

Inverting the structure factor equation

Since the atomic form factor is a reflection of the electron density, one could write a the expression for the structure factor in continuous form (rather than for discrete points):

$$F_{hkl} = \int_{\text{cell}} \rho(xyz) \exp[2\pi i(hx + ky + lz)]$$

where $\rho(xyz)$ represents the electron density at point (xyz) in the unit cell and the integration is performed for all points in the cell.

Assume that F_{hkl} can be measured. Then $\rho(xyz)$ can be obtained through the Fourier transform of F_{hkl} .

$$\rho(xyz) = \frac{1}{V} \int F_{hkl} \exp[-2\pi i(hx + ky + lz)]$$

where V is the volume of the unit cell. One could write this as the summation:

$$\rho(xyz) = \frac{1}{V} \sum_{h,k,l} F_{hkl} \exp[-2\pi i(hx + ky + lz)]$$

But we remember that the vector F_{hkl} can be written in terms of its amplitude and phase:

$$F_{hkl} = |F_{hkl}| \exp[i\phi(hkl)]$$

where $\phi(hkl)$ is the phase associated with the point in reciprocal space associated with the coordinates (hkl) . This means

$$\rho(xyz) = \frac{1}{V} \sum_{h,k,l} |F_{hkl}| \exp[i\phi(hkl)] \exp[-2\pi i(hx + ky + lz)]$$

The structure factor has units of electrons and the density $\rho(xyz)$ has units of electrons \AA^{-3} . The summation is over all h, k and l values. The summation must be carried out on as fine a grid of x, y and z points as possible to obtain a smooth electron density distribution in the unit cell. Where the electron density is concentrated, atoms are found.

Solving a crystal structure

Assume you have a crystal about which you know nothing. This crystal diffracts X-rays and you collect as complete a 3D set of diffraction data as possible. The question is whether the diffraction data has all the information necessary to completely determine the structure of the crystal. Can the diffraction pattern be used to locate all atoms in the unit cell, and their identities established. The answer is yes, at least in most cases. This despite the fact that phase information is not available in the diffraction pattern.

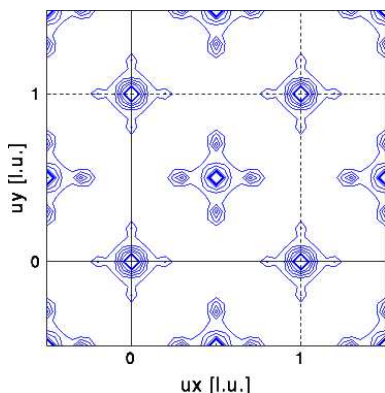
Two methods are commonly used to get around the phase problem. The first is the use of so-called Patterson synthesis and the second, more widely used class of tools are referred to as Direct Methods.

Patterson synthesis

The Fourier transform (FT) of the observed diffraction beam amplitudes $|F|$ gives the correct electron density, but it requires a knowledge of the phases of all the reflections. The FT of the squared amplitudes $|F|^2$ with all phases set to zero is called the Patterson function/synthesis/map:

$$P(xyz) = \frac{1}{V} \sum_{h,k,l} |F_{hkl}|^2 \exp[-2\pi i(hx + ky + lz)]$$

All information required to produce such a transform is available from experimental data.



The Patterson function is periodic and looks just like one might expect the electron density to look. The peaks in the Patterson are *not* peaks in the electron density. Instead, they correspond to a mapping of vectors between pairs of atoms. For every pair of atoms at the positions (x_1, y_1, z_1) and (x_2, y_2, z_2) , there are equal peaks in the Patterson map at the the position $(x_1 - x_2, y_1 - y_2, z_1 - z_2)$ and $(x_2 - x_1, y_2 - y_1, z_2 - z_1)$. The relative sizes of the Patterson peaks are proportional to the square of the atomic numbers at the two sites.

In the Patterson map, the strongest peaks are always at the origin, corresponding to vectors between atoms and themselves. If there are n atoms, there are $n^2 - n$ other peaks. Many of these

are difficult to resolve. If there are a few heavy atoms in the structure however, these form pairs that give rise to strong peaks and their positions can be guessed.

Once heavy atoms are located, one can calculate the forward Fourier transform (which is precise) to obtain a set of calculated structure factors: $F_{hkl, \text{calc}}$. These are compared with the observed structure factors F_{hkl} and the model is improved using an iterative procedure.

Direct methods

In direct methods, a few strong I_{hkl} are chosen and their phases are assigned at random. Then relationships between the phases are sought for, and the phases constantly modified until a consistent set is obtained. This allows initial $F_{hkl, \text{calc}}$ to be obtained. The structure is improved thereon.

The Debye-Waller Factor (after Kittel)

The structure factor F has the term

$$f_j \exp(-i\vec{q} \cdot \vec{r}_j) \quad (1)$$

where f_j is the form factor of the atom j at a site described by \vec{r}_j , and \vec{q} is the scattering wave vector ($|\vec{q}| = 2\pi/d$). Now in a real crystal, the atom j is not precisely at the site described by \vec{r}_j , but rather, oscillating about some mean position so that we can write

$$\vec{r}_j(t) = \vec{r}_j + \vec{u}(t) \quad (2)$$

where $\vec{r}_j(t)$ describes the instantaneous position of the atom at time t , and $\vec{u}(t)$ is the displacement at that time. \vec{r}_j is then the mean position of the atom, or the “frozen” position.

The thermal average of the structure factor is written using $\langle \text{quantity} \rangle$, so that the term in the structure factor expression becomes:

$$f_j \exp(-i\vec{q} \cdot \vec{r}_j) \langle \exp(-i\vec{q} \cdot \vec{u}) \rangle \quad (3)$$

we expand the term $\langle \exp(-i\vec{q} \cdot \vec{u}) \rangle$ as a series:

$$\langle \exp(-i\vec{q} \cdot \vec{u}) \rangle = 1 - i\langle \vec{q} \cdot \vec{u} \rangle - \frac{1}{2} \langle (\vec{q} \cdot \vec{u})^2 \rangle + \dots \quad (4)$$

Now $\langle \vec{q} \cdot \vec{u} \rangle = 0$ since the displacements are uncorrelated and random. If we drop higher terms in the expansion, we have the term in the structure factor $\frac{1}{2} \langle (\vec{q} \cdot \vec{u})^2 \rangle$, which can be simplified:

$$\langle (\vec{q} \cdot \vec{u})^2 \rangle = q^2 \langle u^2 \rangle \langle \cos^2 \theta \rangle = \frac{1}{3} \langle u^2 \rangle q^2 \quad (5)$$

The term $\frac{1}{3}$ arises by taking the geometrical average of $\cos^2 \theta$ over a sphere.

We now write:

$$\exp(-\frac{1}{6} \langle u^2 \rangle q^2) = 1 - \frac{1}{6} \langle u^2 \rangle q^2 + \dots \quad (6)$$

It can be shown from comparing (4) and (6) that for a harmonic oscillator, all the individual terms in the two are identical. This means that the structure factor term is now:

$$f_j \exp(-i\vec{q} \cdot \vec{r}_j) \exp(-\frac{1}{6} \langle u^2 \rangle q^2) \quad (7)$$

The intensity of the scattered radiation comes by squaring terms such as the one in equation (7):

$$I \sim f_j \exp(-i\vec{q} \cdot \vec{r}_j) f_j \exp(i\vec{q} \cdot \vec{r}_j) \exp(-\frac{1}{3}\langle u^2 \rangle q^2) = I_0 \exp(-\frac{1}{3}\langle u^2 \rangle q^2) \quad (8)$$

Where I_0 is the intensity from a rigid lattice.

The intensity drop-off in x-ray diffraction with increasing $|\vec{q}| = 2\pi/d$ or $s = |\vec{q}|/4 = \frac{\sin \theta}{\lambda}$ therefore arises both from the drop in the form factor as well as the Debye-Waller factor.

In the case of neutron diffraction, the drop off is purely due to the Debye-Waller factor.

What causes the motion of the atom? There is both a phonon contribution that increases as temperature increases, as well as the quantum-mechanical zero-point motion.

There are other ways in which the Debye-Waller factor is presented. In crystallography, it is common to write:

$$f = f_0 \exp[-B(\frac{\sin \theta}{\lambda})^2] \quad (9)$$

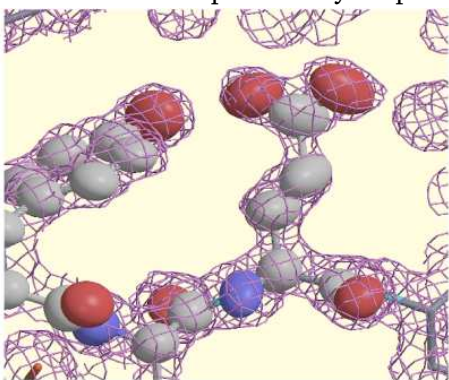
Where $B = 8\pi^2 U$ and has the units of \AA^2 . Here $U = \langle u^2 \rangle$, the mean-squared displacement of the atom with respect to its equilibrium position. B is called the atomic temperature factor, and typical values are between 0.20 and 3.0 \AA^2 .

When written as above, the assumption is that the thermal parameter is *isotropic*, or spherical. In crystals, it is a tensor quantity, represented by the matrix:

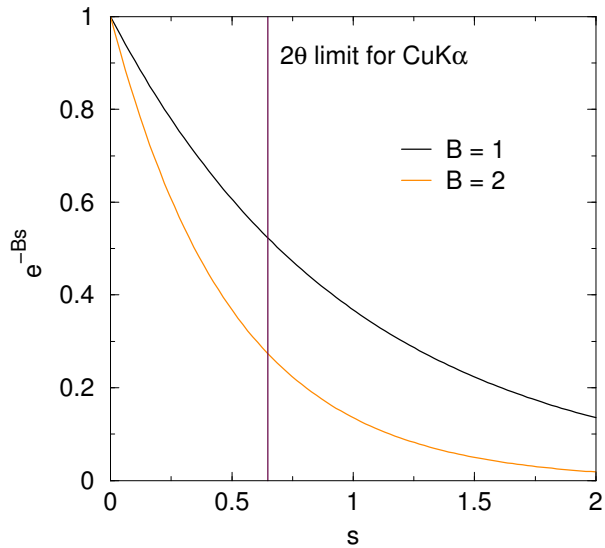
$$\mathbf{U} = \begin{pmatrix} U_{11} & U_{12} & U_{13} \\ 0 & U_{22} & U_{23} \\ 0 & 0 & U_{33} \end{pmatrix}$$

Depending on site symmetry of the atom, some of the terms in the matrix can be redundant.

Experimentally determined thermal parameters can be used to plot so-called thermal ellipsoids. Here are some 50% probability ellipsoids from a protein crystal:



The Debye-Waller factor starts making its presence felt at high angles:



The Lorentz correction (after Giacovazzo)

Diffraction arises when points in the reciprocal lattice are intersected by the Ewald sphere. In experiments, for different points in the reciprocal space, the time that the the points spend satisfying the Bragg condition (crossing the Ewald sphere) is not constant across all the points. This requires a small correction to the intensity, usually a function of 2θ . In certain simple cases (meaning simple diffraction geometries):

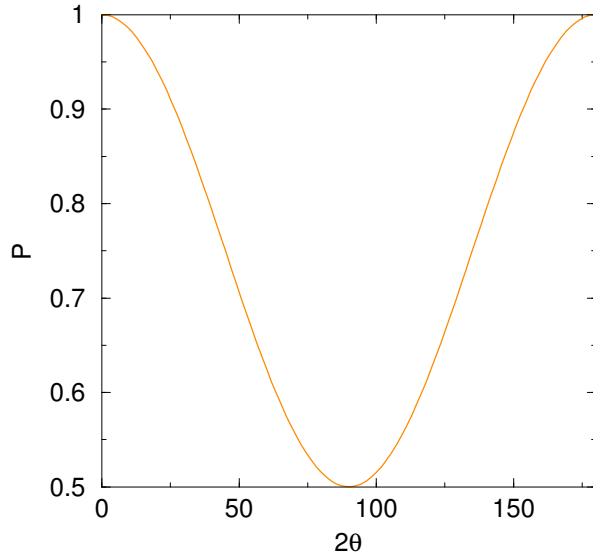
$$L = \frac{1}{\sin 2\theta}$$

The Polarization Correction after Giacovazzo)

X-rays incident on a crystal or powder in an x-ray experiment may or may not be polarized. The reflected X-rays, coming out from the crystal/powder are polarized however. This affects the intensity. If the radiation is not monochromatized (no crystal on the incident side), the polarization correction takes on the form:

$$P = \frac{1}{2}(1 + \cos^2 2\theta)$$

This is the simplest case, and is plotted below:



Usually, the Lorentz and Polarization corrections are grouped together as LP , and the correction for intensity is:

$$|F_{\text{relative}}| = \sqrt{\frac{I_{hkl}}{LP}}$$

This follows Stout and Jensen.

The Rietveld formula (after Giacovazzo)

Powder x-ray diffraction data is step scanned to obtain a large number of observed intensities (y_{io}). The calculated intensities are:

$$y_{ic} = s \sum_k LP_k |F_k|^2 G(\Delta\theta_{ik}) + y_{ib}$$

where s is the scale factor, LP_k is the Lorentz-Polarization factor, F_k is the structure factor, and y_{ib} is the background intensity. $\Delta\theta_{ik} = 2\theta_i - 2\theta_k$ where $2\theta_k$ is the scattering angle where the Bragg condition is fulfilled (corrected for instrumental errors), and $2\theta_i$ represents neighboring regions. $G(\Delta\theta_{ik})$ is then the profile function.

The profile function given by Caglioti requires three parameters, u , v and w :

$$\Gamma(\theta) = \sqrt{u \tan^2(\theta/2) + v \tan(\theta/2) + w}$$

Where $\Gamma(\theta)$ is the FWHM.

For a pseudo-Voigt peakshape (Gaussian + Lorentzian), the intensity looks like:

$$I_{PV}(\theta_1; \theta_2 - \theta_1) = \frac{2\sigma\Gamma(\theta_1)}{\pi[\Gamma(\theta_1)^2 + 4(\theta_1 - \theta_2)^2]} + (1 - \sigma) \sqrt{\frac{4 \ln(2)}{\pi\Gamma(\theta_1)^2}} \exp\left(\frac{-4 \ln(2)(\theta_1 - \theta_2)^2}{\Gamma(\theta_1)^2}\right)$$

The structural model (reflected in F_{hkl} is improved until the fit is good. The factor that is minimized is the residual:

$$S = \sum w_i |y_{io} - y_{ic}|^2$$

where w_i is some suitable weighting.

Anomalous scattering (after Giacobozzo)

Electrons are quantum creatures that can be considered as natural oscillators. The idea that x-rays scatter off electron density like the atoms were points is accurate only if there is no resonance condition between the x-ray and the quantum states of electron. This is not always true. The correct expression for the atomic form factor is:

$$f = f_a + \Delta f' + f''$$

where $\Delta f'$ and f'' are called the real and imaginary dispersion corrections. Please see the handout.

Anomalous scattering etc.

Mostly following Als-Nielsen and Morrow, and Giacobozzo

In normal practice, the scattering of x-rays from atoms in the process of diffraction is considered to be purely kinematic, associated with changes in momenta, but no absorption or emission of energy. Usually, this is an accurate assumption, and the form factor f for the different atoms in the crystal can be written:

$$f(\vec{q})$$

In some interesting cases however, (rare in the lab, but more common with synchrotron x-ray sources where x-ray energies/wavelengths can be tuned) the correct expression is:

$$f(\vec{q}, \omega) = f(\vec{q}) + f'(\omega) + if''(\omega)$$

where f' and f'' are the real and imaginary parts of the dispersion correction. ω is the frequency of the x-ray wavelength, and correspondingly, the x-ray energy is $E = \hbar\omega$. The dispersion corrections are energy (wavelength) dependent, but usually do not depend on \vec{q} , the scattering vector.

It is important to note that even when f' and f'' are finite, the scattering is still elastic. The wavelength of scattered x-rays does not change when f' and f'' are finite, it is just that the simple form factor $f(\vec{q})$ no longer accurately describes scattering.

In the simplest treatments, the electromagnetic component of the x-ray is treated as one oscillator and an electron on the scattering atom is treated as another. The two oscillators couple when their frequencies are closely matched — when a *resonance* condition is fulfilled.

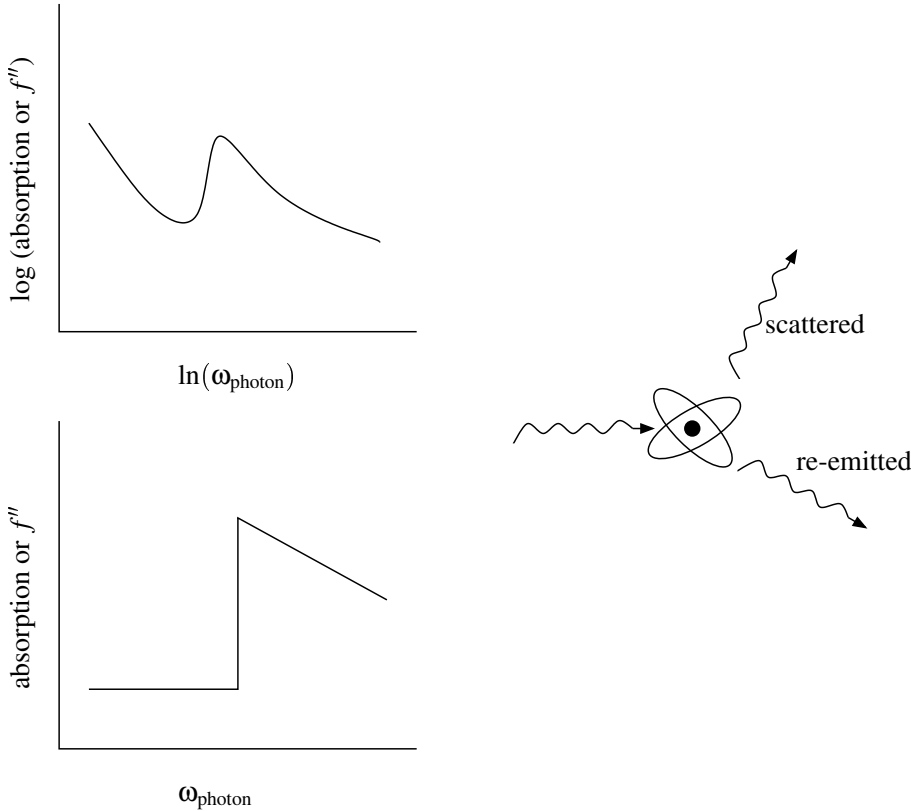
In the figure given below, f'' as a function of the x-ray photon energy (frequency) is plotted schematically for an element with an *x-ray absorption edge* in the energy range of interest. The resonance condition for the two oscillators to couple is met at the edge. Far from the edge, the scattering is as though f'' and f' are zero.

In the process of absorption, two important things happen. The first is the contribution of f' which is to effectively change the atomic number of the scattering atom. The second is the effect of F'' which is to introduce a phase difference into the scattered photon.

The absorption of the photon can be monitored from the fluorescence intensity. The absorption is related to f'' . f' can be obtained from f'' using the Kramers-Kronig relationship:

$$F'(\omega) = \frac{2}{\pi} \mathcal{P} \int_0^\infty \frac{\omega' f''(\omega')}{(\omega'^2 - \omega^2)} d\omega'$$

Where \mathcal{P} refers to the principal value.



Where does anomalous scattering show up ?

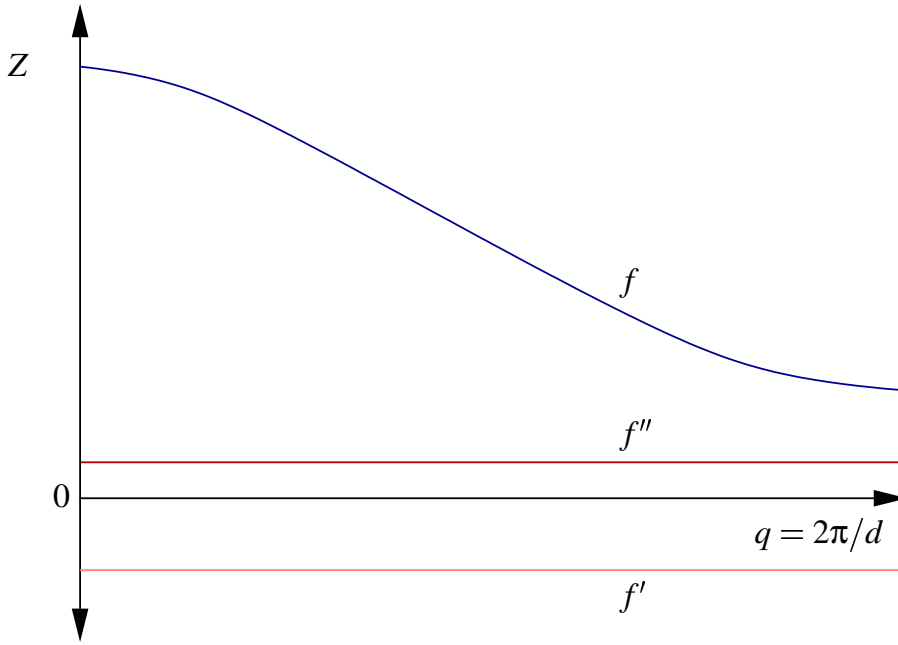
For CuK α lab x-rays, the element holmium has an L₃ edge that is quite close in energy (1.5368 Å). This gives the anomalous scattering coefficients:

CuK α_1 ($\lambda = 1.5406$ Å)	$f' \sim -15.41$	$f'' \sim 3.70$
CuK α_2 ($\lambda = 1.5444$ Å)	$f' \sim -14.09$	$f'' \sim 3.72$

In addition, the L₂ absorption edge is close to CuK β , and this gives:

CuK β ($\lambda = 1.3922$ Å)	$f' \sim -11.78$	$f'' \sim 8.75$
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So typically, Holmium will seem about 14 electrons “lighter” when diffraction is performed using copper radiation. Ho can thus be distinguished from Dy or Er, even though the Z 's are separated only by 1 electron. Note that these effects will be most visible at high $q = 2\pi/d$ when the normal f would have died out.



Friedel's law and anomalous scattering

Consider the scattering from two different atoms, one at the origin and one at x . The total scattering amplitude is:

$$A(q) = f_1 + f_2 \exp(iqx)$$

and the intensity is:

$$I(q) = [f_1 + f_2 \exp(iqx)][f_1 + f_2 \exp(-iqx)] = f_1^2 + f_2^2 + 2f_1f_2 \cos(qx)$$

The cosine function is even, meaning that $I(q) = I(-q)$. Therefore, one cannot tell from the scattering whether an atom 1 is on the left and atom 2 on the right or *vice-versa*.

However, imagine the case where f' and f'' are finite. Then for each atom, we must write the form factor as

$$f_j = f_j^0 + f_j' + if_j'' ; j = 1, 2$$

This is expressed more conveniently as

$$f_j = |f_j| \exp(i\phi_j)$$

Using this, the amplitude of the two-atom problem now becomes:

$$A(q) = |f_1| \exp(i\phi_1) + |f_2| \exp(i\phi_2) \exp(iqx)$$

and the intensity is:

$$I(q) = |f_1|^2 + |f_2|^2 + 2|f_1||f_2| \cos(qx + \phi_1 - \phi_2)$$

Since $\phi_1 \neq \phi_2$, it follows that:

$$I(q) \neq I(-q)$$

Friedel's law says that the scattered intensity from a Friedel pair is centrosymmetric. Friedel pairs are Bragg reflections that are related by inversion about the origin; the pair of reflections arising from hkl and $\bar{h}\bar{k}\bar{l}$. The statement of Friedel's law can be written:

$$|F_{hkl}| = |F_{\bar{h}\bar{k}\bar{l}}| \quad ; \quad \phi_{hkl} = -\phi_{\bar{h}\bar{k}\bar{l}}$$

When there is an anomalous component, this law breaks down.

When the structure is centrosymmetric, and atom 1 sits at $\pm x_1$ and atom 2 at $\pm x_2$, then the unit cell structure factor is:

$$\begin{aligned} F &= |f_1| \exp i(\phi_1 + qx_1) + |f_1| \exp i(\phi_1 - qx_1) \\ &+ |f_2| \exp i(\phi_2 + qx_2) + |f_2| \exp i(\phi_2 - qx_2) \\ &= [|f_1|2 \cos(qx_1)] \exp(i\phi_1) + [|f_2|2 \cos(qx_2)] \exp(i\phi_2) \end{aligned}$$

The intensity is then:

$$\begin{aligned} I(q) = |F|^2 &= 4|f_1|^2 \cos^2(qx_1) + 4|f_2|^2 \cos^2(qx_2) \\ &+ 8|f_1|^2 |f_2|^2 \cos^2(qx_1) \cos^2(qx_2) \cos(\phi_2 - \phi_1) \end{aligned}$$

The intensity is once again an even function of q .

Applications

ZnS blende (1928)

The intensity of the Bragg reflection from the 111 zinc blende crystal face depends on whether the surface that \vec{q} is incident on is all Zn or all S.

Bijvoet's 1950 experiment on sodium rubidium tartarate

Allowing absolute configuration to be determined.

MAD phasing

Using a synchrotron source, where x-ray wavelengths are tunable, one can obtain data sets from single crystals at multiple wavelengths. If some of the sets correspond to anomalous scattering from different atoms in the structure, the phase problem can be avoided.