

Materials 286C/UCSB: Class VI — Structure factors (continued), the phase problem, Patterson techniques and direct methods

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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:

$$F_{hkl} = f_{\text{Cs}} \exp[2\pi i(h \cdot 0 + k \cdot 0 + l \cdot 0)] + f_{\text{Cl}} \exp[2\pi i(h \frac{1}{2} + k \frac{1}{2} + l \frac{1}{2})]$$

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:

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

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

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

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

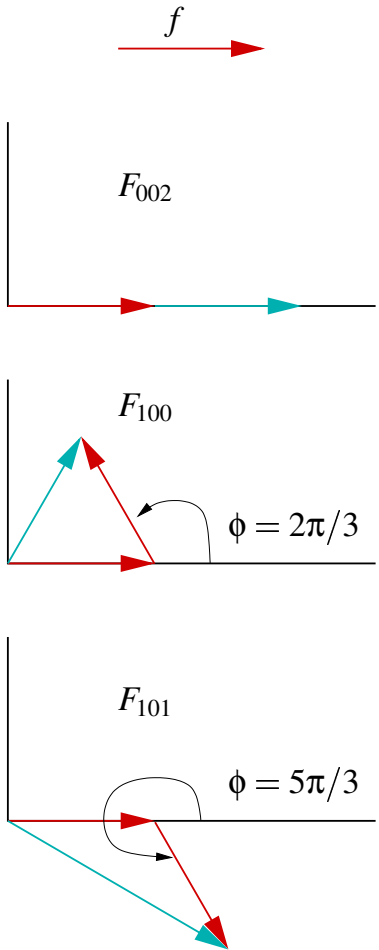
The corresponding intensities are obtained from

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

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, it's 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:

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

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.

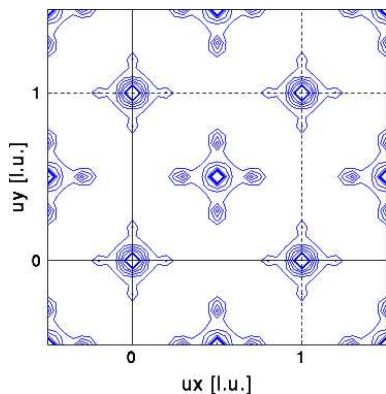
Two methods are commonly used to get around the phase problem. The first is the use of so-called Patterson synthesis and the second, more widely used class of tools are referred to as Direct Methods.

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: $F_{hkl,calc}$. 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 $F_{hkl,calc}$ to be obtained. The structure is improved thereon.