Materials 286C/UCSB: Class V — The form and structure factors, intensities, and the phase problem, and systematic absences

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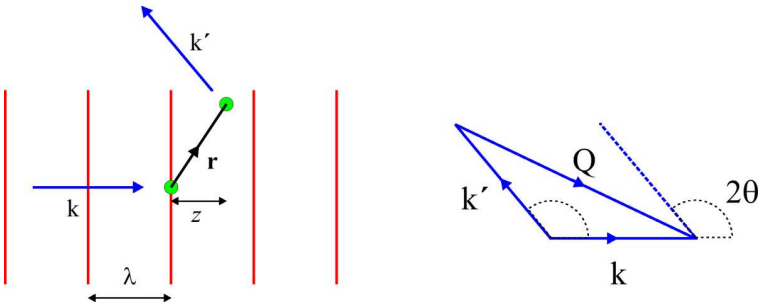
The atomic form factor

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:

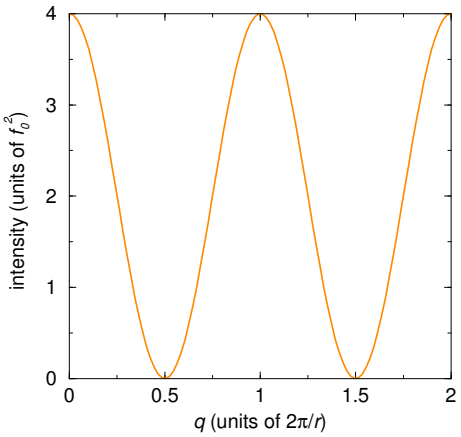
$$|\vec{q}| = (\frac{4\pi}{\lambda}) \sin\theta = \frac{2\pi}{d}$$

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 enclose.

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

where $e^{i\vec{q}\cdot\vec{r}}$ is the usual phase factor. The limiting conditions are $\vec{q} \to 0$ when $f = Z$ (where Z is the atomic number), and $\vec{q} \to \infty$ 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 that the form factors of "compact" atoms.

Tabulations of the form factor

The calculated[1] 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

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

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:

$$\begin{aligned}\left\langle \left| \sum_{j=1}^{N} f_j e^{i\vec{q}\cdot\vec{r}_j} \right| \right\rangle_{\text{orient. av.}} &= |f_1|^2 + |f_2|^2 + \ldots |f_N|^2 \\ &+ 2f_1 f_2 \frac{\sin(qr_{12})}{qr_{12}} + \ldots + 2f_1 f_N \frac{\sin(qr_{1N})}{qr_{1N}} + \ldots \\ &+ 2f_2 f_3 \frac{\sin(qr_{23})}{qr_{23}} + \ldots + 2f_2 f_N \frac{\sin(qr_{2N})}{qr_{2N}} + \ldots \\ &+ 2f_{N-1} f_1 \frac{\sin(qr_{N-1,1})}{qr_{N-1,1}} + \ldots + 2f_{N-1} f_N \frac{\sin(qr_{N-1,N})}{qr_{N-1,N}}\end{aligned}$$

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.