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:

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

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:

$$f(\vec{q}) = \frac{\text{amplitude of scattering by atom}}{\text{amplitude of scattering by a single electron}}$$

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 than 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:

<table>
<thead>
<tr>
<th>$a_1$</th>
<th>$b_1$</th>
<th>$a_2$</th>
<th>$b_2$</th>
<th>$a_3$</th>
<th>$b_3$</th>
<th>$a_4$</th>
<th>$b_4$</th>
<th>$c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.2915</td>
<td>3.2133</td>
<td>3.0353</td>
<td>32.333</td>
<td>1.9891</td>
<td>0.6785</td>
<td>1.5410</td>
<td>81.6937</td>
<td>1.1407</td>
</tr>
</tbody>
</table>

\(^1\)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:

\[
\left| \sum_{j=1}^{N} f_j e^{iq \cdot r_j} \right|_{\text{orient. av.}}^2 = |f_1|^2 + |f_2|^2 + \ldots |f_N|^2
\]

\[
+ 2f_1f_2 \frac{\sin(qr_{12})}{qr_{12}} + \ldots + 2f_1f_N \frac{\sin(qr_{1N})}{qr_{1N}} + \ldots
\]

\[
+ 2f_2f_3 \frac{\sin(qr_{23})}{qr_{23}} + \ldots + 2f_2f_N \frac{\sin(qr_{2N})}{qr_{2N}} + \ldots
\]

\[
+ 2f_{N-1}f_1 \frac{\sin(qr_{N-1,1})}{qr_{N-1,1}} + \ldots + 2f_{N-1}f_N \frac{\sin(qr_{N-1,N})}{qr_{N-1,N}}
\]

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.