Determination of Crystal Structures:
Elementary Theory of X-rays (and maybe Neutron) Diffraction

Simplified presentation:

Let us suppose we have a small crystal like the one below:

Case I. A crystal is made up of many identical atoms.
Consider scattering of X-rays of one atom

\[ E(\vec{x}, t) = \text{Re}[E_0 e^{i \vec{k} \cdot \vec{x} - i \omega t}] \]
Simplified theory: Suppose atom is located at the origin. We have incident electric field which hits atom. The atom produces a scattered wave which has amplitude

$$\vec{E}_{\text{scatt}} = \text{Re} \left\{ E_0 e^{-i \omega t} f \frac{e^{i k r}}{r} \right\}$$

where $f$ is the "scattering amplitude" of the $n$th atom. I will just quote the result for X-ray scattering:

$$\vec{E}_{\text{scatt}}(\vec{x}, t) = \text{Re} \left\{ \frac{\vec{n} \times (\vec{n} \times \vec{E}_0)}{r} f(\vec{q}) \frac{e^{i k r - i \omega t}}{r} \right\}$$

where the geometry is as below:

$$f(\vec{q}) = \frac{e^2}{m c^2} n_e(\vec{q})$$

$$n_e(\vec{q}) = \int m_e(\vec{r}) e^{i \vec{q} \cdot \vec{r}} d^3r$$

$m_e(\vec{r}) = \text{electron number density of atom}$
This is shown in typical (Jackson) E+M book.

\[ \hat{q} = \hat{k}' \times \hat{r} \] and \( \hat{k}' = k \hat{n} \)

Scattered power is therefore

\[ \left( \frac{dP_{\text{scatt}}}{d\Omega} \right) = \left\{ \frac{c|\vec{E}_{\text{scatt}}|^2}{8\pi} \cdot r^2 \right\} \]

where the bracket means time-average,

and thus

\[ \frac{dP_{\text{scatt}}}{d\Omega} = \frac{c}{8\pi} \left| \hat{m} \times (\hat{n} \times \vec{E}_0) \right|^2 \left\{ \frac{1}{r^2} \right\} \]

Polarization "atomic form factor" 1

This is for one atom.

Now suppose we have a monatomic crystal.

The scattering amplitude off the ith atom is

\[ \vec{E}_{\text{scatt}}(x,t) = \text{Re} \left\{ \hat{n} \times (\hat{n} \times \vec{E}_0) f(\hat{q}) \hat{r}_i \cdot e^{-ik\cdot\hat{r}_i - i\omega t} \right\} \]

where again \( k = \frac{\omega}{c} \), \( \hat{r}_i \) = position of ith atom, and geometry is as shown below:
Then \[ \hat{E} = E_0 e^{i k \cdot x - i \omega t} \]

Suppose \[ |x| \gg |\hat{r}_i| \]

Then \[ \frac{1}{|x - \hat{r}_i|} \sim \frac{1}{|x|} \sim \frac{1}{r} \]

But in numerator we have \[ |x - \hat{r}_i| \sim r - \hat{n} \cdot \hat{r}_i \]

So \[ e^{i k |x - \hat{r}_i|} \sim e^{i k r - k \hat{n} \cdot \hat{r}_i} \sim e^{i k r - \hat{n} \cdot \hat{r}_i} \]

\[
\frac{dP_{\text{scatt}}}{d\Omega} \text{ involves the factor}
\]

\[
\sum_i e^{ik \cdot \hat{r}_i - ik' \cdot \hat{r}_i} e^{i k r' - i \omega t}
\]

\[
= \sum_i e^{-i \hat{r}_i \cdot \hat{r}_i} e^{i k r - i \omega t}
\]
Therefore
\[
\frac{dP_{\text{scatt}}}{d\Omega} = \frac{e^{-i\mathbf{q} \cdot \mathbf{R}}}{8\pi} \left| f(\mathbf{q}) \right|^2 \left| \sum_i e^{-i\mathbf{q} \cdot \mathbf{R}_i} \right|^2
\]

Phase factor

Now, finally, let \( \mathbf{R}_i = \mathbf{R} = \text{Bravais lattice vector} \)

Then \[
\left| \sum_i e^{-i\mathbf{q} \cdot \mathbf{R}_i} \right| = \left| \sum_i e^{-i\mathbf{q} \cdot \mathbf{R}} \right|
\]

\[
= N^2 \quad \mathbf{q} = \mathbf{K}
\]

\[
\approx 20 \quad \mathbf{q} \neq \mathbf{K} \quad \text{(since phase factors random)}
\]

No scattering unless \( \mathbf{q} = \mathbf{K} \).

E.g. Bragg geometry.
Typical geometries:

Bragg geometry:

\[ k' - k = 2k = n\lambda \]

\[ |k' - k| = |k| = K = 2k\sin\theta = \frac{2\omega}{c}\sin\theta \]

\[ = \frac{4\pi}{\lambda} \sin\theta \]

\[ \sin\theta = \frac{2\lambda k}{4\pi} \]

Limited # of allowed angles

Pattern on a screen

\[ \text{symmetry of spots on screen allows you to tell structure} \]
More than one atom per primitive cell:

\[ \frac{dP_{\text{scat}}}{d\Omega} = \frac{e}{8\pi} \left| \hat{n} \times (\hat{n} \times \hat{E}_0)^2 \right| \left\{ \sum_{\text{all atoms}} Z \frac{f_i(\mathbf{q}) e^{-i\mathbf{q} \cdot \mathbf{R}_j}}{2} \right\}^2 \]

\[ = \left| \sum_{\text{atoms}} \sum_{j=1}^{N_a} f_i(\mathbf{q}) e^{-i\mathbf{q} \cdot \mathbf{R}_j} \right|^2 \]

\[ = N^2 \left( \sum_{j=1}^{N_a} f_i(\mathbf{q}) e^{-i\mathbf{q} \cdot \mathbf{R}_j} \right)^2 \]

\[ \text{sometimes called} \]

\[ |S(\mathbf{K})|^2 \text{ where } S(\mathbf{K}) = \text{geometric structure factor} \]

Intriguing example:

Diamond structure:

\[ f_i(\mathbf{K}) = \text{same for both atoms} \]

\[ \hat{\mathbf{b}}_1 = 0, \quad \hat{\mathbf{b}}_2 = \frac{a}{4} (\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}) \]

\[ \mathbf{K} = \frac{2\pi}{a} (n_x \hat{\mathbf{x}} + n_y \hat{\mathbf{y}} + n_z \hat{\mathbf{z}}) \]

\[ n_x \text{'s all even or all odd} \]
\[|S(K)|^2 = |1 + e^{i \frac{a}{4}(K_x + K_y + K_z)}|^2\]

vanishes for some values of \(K\)

lots of info in X-ray scattering lines.

Comment:

\[\frac{dP}{d\Omega} \propto (\text{ Nel}(\frac{K}{a}))^2\]

largest for heavy elements

\(\Rightarrow\) Pb good for X-ray shield

Be """" window

Note also,

scattering off electrons, not ions

(constant) (since much heavier)
Example:

X-ray diffraction from [100] face of a simple cubic crystal.

\[ \overrightarrow{k'} = \frac{\omega}{c} (x \cos \theta + z \sin \theta) \]

\[ \overrightarrow{k} = \frac{\omega}{c} (x \cos \theta - z \sin \theta) \]

\[ \overrightarrow{k'} - \overrightarrow{k} = 2 \frac{\omega}{c} \frac{z}{2} \sin \theta \]
But $\frac{\omega}{c} = \frac{2\pi}{a}$ so

$$4\pi^2 \frac{\lambda}{\lambda} \hat{x} \sin \theta = \vec{K}$$

The $\vec{K}$ vectors for simple cubic lattice are

$$\frac{2\pi}{a} (n_x \hat{x} + n_y \hat{y} + n_z \hat{z})$$

For this type of incidence, we need $n_x \neq 0$, $n_y = n_z = 0$, so

$$\frac{4\pi}{\lambda} \hat{x} \sin \theta = \frac{2\pi}{a} m_x \hat{x} \quad \text{or} \quad \eta \lambda = 2a \sin \theta$$

Bragg condition

What if incident wave vector is

$$\vec{K} = \frac{\omega}{c} \left( -\frac{\hat{x} \sin \theta + \hat{z} \cos \theta}{\sqrt{2}} \right)$$

$$\vec{K}' = \frac{\omega}{c} \left( +\frac{\hat{x} \sin \theta + \hat{z} \cos \theta}{\sqrt{2}} \right)$$

again

$$\vec{K}' - \vec{K} = \frac{2\omega}{c} \frac{\sin \theta}{2} = \frac{2\pi}{a} m_x \hat{x} \hat{z}$$

$$\Rightarrow \eta \lambda = 2a \sin \theta \quad \text{once again}$$
Bragg condition:

\[ d = \text{dist. between lattice planes} \]

Path length difference must add up to integer #

or wavelengths \( \Rightarrow 2d \sin \theta = n \lambda \)

(as before)

(Equivalent to reciprocal lattice vector condition

since \( d = \frac{2\pi}{K} \) where \( K \) is a reciprocal lattice vector \( \perp \) to planes)

Crystal face symmetry from a different geometry.

Incident beam \( \rightarrow \) Crystal

Screen on which spots are detected
More on diamond:

If \( a \) is conventional cube edge, then reciprocal lattice is bcc with conventional cube edge \( \frac{4\pi}{a} \).

I.e. \( \frac{2\pi}{a} (n_x \hat{x} + n_y \hat{y} + n_z \hat{z}) \)

where \( n_x, n_y, n_z \) are either all odd or all even.

Then \( e^{i \frac{a}{4} (K_x + K_y + K_z)} = \exp \left\{ i \frac{\pi}{2} (n_x + n_y + n_z) \right\} \)

\( = 1 \) \( n_x + n_y + n_z \) divisible by 4

\( = -1 \) \( " " " " \) divisible by 2, but not by 4

\( = \pm i \) \( n_x + n_y + n_z \) odd.

For second case, no (very little) scattering.
**β - Brass: Cu Zn**

![Crystal structure diagram]

- **Low temperature phase. sc Bravais lattice**
  - with basis of two atoms
  
  \[ \mathbf{b}_1 = 0 \quad (\text{Cu}) \]
  \[ \mathbf{b}_2 = \frac{a}{2} (\mathbf{x} + \mathbf{y} + \mathbf{z}) \quad (\text{Zn}) \]

- "Atomic structure factor"

\[ S(\mathbf{K}) = \left| f_{\text{Cu}} e^{i\mathbf{K} \cdot \mathbf{b}_1} + f_{\text{Zn}} e^{i\mathbf{K} \cdot \mathbf{b}_2} \right|^2 \]

where \( \mathbf{K} = \frac{2\pi}{a} (n_x \mathbf{x} + n_y \mathbf{y} + n_z \mathbf{z}) \) for \( n_x, n_y, n_z \in \mathbb{Z} \)

So \( e^{i\mathbf{K} \cdot \mathbf{b}_2} = \exp\left[ i\pi(n_x n_y n_z) \right] = (-1)^{n_x n_y n_z} \)

- \( n_x + n_y + n_z \) even:

\[ S(\mathbf{K}) = \left| f_{\text{Cu}} + f_{\text{Zn}} \right|^2 \]
$m_x + n_y + n_z \text{ odd:}$

$$S(i^2) = \left| f_{cu} - f_{zn} \right|^2$$

"superlattice lines"

At high temperatures, lattice randomizes, one can say that you have an "average" atom at each site — superlattice lines disappear.
Scattering X-section

\[ \alpha \sim |f_{av}(K)|^2 \left| 1 + e^{iK \cdot b} \right|^n \]

\[ = 4 |f_{av}(K)|^2 \quad n_x + n_y + n_z \text{ even} \]

\[ = 0 \quad n_x + n_y + n_z \text{ odd} \]

(some of lattice lines disappear)

\[ \text{Observed:} \]

\[ \frac{d \Omega}{d \mathbf{K}} \]

\[ (\mathbf{K} = \frac{2 \pi}{a} (x \hat{a} + y \hat{b} + z \hat{c})) \]

\[ T_0 \quad \text{T = temp} \]

"order-disorder transition"

Basically, this happens because at high T, we have a BCC Bravais lattice with half the density of pts in reciprocal space