Scattering from a crystal with basis

So far we have considered scattering from a crystal lattice described by lattice vectors $\vec{a}_1, \vec{a}_2, \vec{a}_3$. Given $\vec{s} = \vec{k} - \vec{k}_0$, the key quantity in determining the intensity of the scattered X-rays is the lattice structure factor

$$S = \sum_{l_1=1}^{N} \sum_{l_2=1}^{N} \sum_{l_3=1}^{N} e^{i\vec{s} \cdot \vec{a}_l} e^{-i\vec{s} \cdot \vec{a}_l}$$

and for a lattice with a very large number of sites ($N \to \infty$) we get

$$S \neq 0 \text{ only when } \begin{cases} \vec{s} \cdot \vec{a}_1 = \frac{\hbar}{2\pi} \\
\vec{s} \cdot \vec{a}_2 = \frac{\kappa}{2\pi} \\
\vec{s} \cdot \vec{a}_3 = \frac{l}{2\pi} \end{cases}$$

This formalism is quite general provided that $\vec{a}_1, \vec{a}_2, \vec{a}_3$ are related to a primitive cell - one which only contains one atom. In such a case, it will take into account interference between scattered waves from every atom in the lattice, since the sum covers all lattice points. We illustrated this for a two dimensional centered rectangular lattice.

One can see that running through all values of $l_1$ and $l_2$ covers all the lattice points. The (1) gives the sum of phases from all points in the lattice.
In some circumstances it is convenient to use vectors corresponding to a standard unit cell which contains more than one atom. In particular we shall see that the lattice structure factor for fcc and bcc lattices can be composed from that of a cubic lattice plus an additional term.

For the centered rectangular lattice, one can use \( \hat{a}_1 \) and \( \hat{a}_2 \) as below:

\[ \hat{a}_1 \quad \hat{a}_2 \]

\[ l_1 = 0 \quad l_1 = 1 \]

But now the sum of Eq. (1) will omit scattering from the centered lattice sites (open circles above). So it will not give a correct expression. The way to correct for this is to regard each lattice site as filled by a pair of atoms, separated by the vector \( \vec{s} \).

One simply places the dark atom at the intersections of the rectangular lattice. The light atom then appears in the center. Clearly this generates the entire lattice. This is called a lattice with basis.

The amplitude of the superposition of all scattered waves is given by:

- The scattered wave that emerges from each unit cell.
- The sum of such scattered waves over all such cells.
With this set up one unit cell produces a wave with amplitude:

$$1 + e^{i\vec{s} \cdot \vec{S}}$$

atom at origin \( \vec{S} \) atom in center.

and when there are more than one atoms in a unit cell with locations from the origin: \( \vec{S}_1, \ldots, \vec{S}_n \) (n atoms in this cell)

$$F = \sum_{j=1}^{n} e^{i\vec{s} \cdot \vec{S}_j}$$  \hspace{1cm} (3)

determines the amplitude of the scattered wave from each cell. This is called the geometrical structure factor.

Example: Square lattice with one point per unit cell.

\[ \text{Here } n=1 \text{ and } \vec{S}_j = 0 \Rightarrow F = 1. \]

Example: Centered rectangular lattice. Let \( \vec{a}_1 = a_1 \hat{x} \)
\[ \vec{a}_2 = a_2 \hat{y} \]

Then one atom is located at \( \vec{S}_1 = 0 \)
The other atom is at \( \vec{S}_2 = \frac{a_1}{2} \hat{x} + \frac{a_2}{2} \hat{y} \)

\( F = 1 + e^{i(s_1 a_1 + s_2 a_2)/2} \)
Why is the geometrical structure factor useful?

The superposition of all scattered waves gives:

\[ \sum_{\text{all } \mathbf{R} \text{ in the lattice}} e^{i \mathbf{s} \cdot \mathbf{R}} \]

But any \( \mathbf{R} \) can be written as:

\[ \mathbf{R} = \begin{cases} l_1 \mathbf{a}_1 + l_2 \mathbf{a}_2 + l_3 \mathbf{a}_3 & \text{for dark lattice sites} \\ l_1 \mathbf{a}_1 + l_2 \mathbf{a}_2 + l_3 \mathbf{a}_3 + \mathbf{S}_1 & \text{for centered lattice sites} \\ l_1 \mathbf{a}_1 + l_2 \mathbf{a}_2 + l_3 \mathbf{a}_3 + \mathbf{S}_n \end{cases} \]

**Exercise:** Check that this is true for the two-dimensional centered rectangular lattice.

Thus

\[ \sum_{\text{all } \mathbf{R}} e^{i \mathbf{s} \cdot \mathbf{R}} = \sum_{l_1, l_2, l_3} e^{i (l_1 \mathbf{a}_1 + l_2 \mathbf{a}_2 + l_3 \mathbf{a}_3) \cdot \mathbf{s}} \left( 1 + e^{i \mathbf{S}_1} + \ldots + e^{i \mathbf{S}_n} \right) \]

\[ \sum_{\text{all } \mathbf{R}} e^{i \mathbf{s} \cdot \mathbf{R}} = FS \]

where \( S \) is the lattice structure factor. Thus the intensity of scattering is:

\[ I \propto |\sum e^{i \mathbf{s} \cdot \mathbf{R}}|^2 \]

\[ \Rightarrow I \propto |F|^2 |S|^2 \] - (4)
So, to determine when scattering occurs we have a condition that stems from the basic lattice:

$$S \neq 0$$

and another condition that stems from the contents of the unit cell.

$$F \neq 0.$$  

**Example:** Centered rectangular two-dimensional lattice. Suppose

$$\hat{a}_1 = a_1 \hat{x},$$

$$\hat{a}_2 = a_2 \hat{y}.$$  

Then

$$\hat{s}_1 = 0,
\hat{s}_2 = \frac{a_1}{2} \hat{x} + \frac{a_2}{2} \hat{y}.$$  

First the lattice scattering factor gives, for $$\hat{s} = \hat{k} - \hat{k}_0$$

$$S \neq 0 \iff \hat{s} \cdot \hat{a}_1 = 2\pi h,$$

$$\hat{s} \cdot \hat{a}_2 = 2\pi k.$$  

for some integers $$h, k.$$  

But with

$$\hat{s} = s_x \hat{x} + s_y \hat{y}$$  

we get:

$$s_x a_1 = 2\pi h \implies s_x = 2\pi h / a_1,$$

$$s_y a_2 = 2\pi k \implies s_y = 2\pi k / a_2.$$  

If the crystal was just a rectangular lattice, we would build the usual picture of reflection off planes perpendicular to $$\hat{s}$$. This gives scattering for any values of $$h, k.$$  

But now with the centered lattice site:

$$F = (1 + e^{i \hat{s}_1 \cdot \hat{s}_2})$$

$$= 1 + e^{i (s_x a_1 + s_y a_2) / 2}.$$  

Thus:

\[ F = 1 + e^{i(2\pi h + 2\pi k)/2} \]

\[ = 1 + e^{i(h+k)\pi} \]

and now we notice that

\[ F = 0 \quad \text{if} \quad h+k \text{ is odd.} \]

\[ F = 2 \quad \text{if} \quad h+k \text{ is even.} \]

Thus whereas for the ordinary lattice, we would have scattering for any values of \( h,k \), the centered lattice eliminates that for \( h+k \) odd.

As a particular example consider \( h=0 \), \( k=1 \). Then the scattering planes are along \( z \).

\[
\begin{array}{c}
\text{Applying the usual Bragg rule for the lattice without the centered points one obtains} \theta \text{ such that for } \lambda \text{ satisfying } \lambda = 2d\sin\theta, \text{ constructive interference occurs. But once the additional sites are in place there are intermediate scattering planes, which will produce out-of-phase waves. These give destructive interference.}
\end{array}
\]
Note that for \( h=k=1 \) the centered points lie in diagonal planes. They are now twice as dense and thus explains \( F=2 \).

**Example: BCC lattice:** We take as lattice vectors
\[ \vec{a}_1 = a\hat{x}, \quad \vec{a}_2 = a\hat{y}, \quad \vec{a}_3 = a\hat{z} \]

To each lattice point we have to attach one more site at
\[ \vec{s}_z = \frac{a}{2}(\hat{x} + \hat{y} + \hat{z}) \quad (\text{with} \quad \vec{s}_1 = \vec{0}) \]

The conditions for strong scattering from the underlying cubic lattice are:
\[ \vec{s}, \vec{a}_i = 2\pi n \]
\[ \vec{s}, \vec{a}_i = 2\pi n \]
\[ \vec{s}, \vec{a}_i = 2\pi n \]

So for \( \vec{s} = s_x\hat{x} + s_y\hat{y} + s_z\hat{z} \), we get:
\[ \frac{s_x}{a} = \frac{2\pi}{a} h, \quad \frac{s_y}{a} = \frac{2\pi}{a} k, \quad \frac{s_z}{a} = \frac{2\pi}{a} l \]

However, the geometrical structure factor is:
\[ F = \sum_{j=1}^{N} e^{i\vec{s}_j \cdot \vec{s}} = 1 + e^{i\frac{2\pi}{a}(s_xa + s_ya + s_za)} / 2 \]
\[ F = 1 + e^{i\frac{2\pi}{a}(h+k+l)} \]

Thus \( F = \begin{cases} 0 & h+k+l \text{ odd} \\ 2 & h+k+l \text{ even} \end{cases} \)
Thus the planes from which scattering occurs are:

<table>
<thead>
<tr>
<th>Simple cubic</th>
<th>fcc</th>
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<tbody>
<tr>
<td>(100)</td>
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etc...
Reciprocal Lattice

We can now consider more general lattice vectors and ask whether we can solve (1). It can always be done explicitly. Consider the vectors, using temporary notation:

\[ \begin{align*}
\vec{b}_1 &= \hat{a}_2 \times \hat{a}_3 \\
\vec{b}_2 &= \hat{a}_3 \times \hat{a}_1 \\
\vec{b}_3 &= \hat{a}_1 \times \hat{a}_2
\end{align*} \]

Now consider

\[ \vec{b}_1 \cdot \hat{a}_i = (\hat{a}_2 \times \hat{a}_3) \cdot \hat{a}_i \]

\text{volume of primitive cell.}

\[ \vec{b}_1 \cdot \hat{a}_2 = \vec{b}_1 \cdot \hat{a}_3 = 0. \]

Using the fact that:

\[ (\hat{a}_2 \times \hat{a}_3) \cdot \hat{a}_i = (\hat{a}_3 \times \hat{a}_1) \cdot \hat{a}_2 = (\hat{a}_1 \times \hat{a}_2) \cdot \hat{a}_3 = \mathcal{L} \]

where \( \mathcal{L} \) is the volume of the unit cell, we see that

\[ \vec{b}_i \cdot \hat{a}_j = \mathcal{L} \delta_{ij} \]

Thus we can choose

\[ \vec{S} = \frac{2\pi h}{\mathcal{L}} \vec{b}_1 + \frac{2\pi k}{\mathcal{L}} \vec{b}_2 + \frac{2\pi l}{\mathcal{L}} \vec{b}_3 \]

Exercise: Verify that (7) solves (1)
The scaling in (7) is not the most convenient. Thus define reciprocal lattice vectors: 

\[ \vec{a}_i^* = \frac{2\pi}{\mathcal{N}} \, \vec{b}_i \] or 

\[ \vec{a}_1^* = \frac{2\pi}{\mathcal{N}} \, \vec{a}_2 \times \vec{a}_3 \]
\[ \vec{a}_2^* = \frac{2\pi}{\mathcal{N}} \, \vec{a}_3 \times \vec{a}_1 \]
\[ \vec{a}_3^* = \frac{2\pi}{\mathcal{N}} \, \vec{a}_1 \times \vec{a}_2 \]  

where 

\[ \mathcal{N} = (\vec{a}_2 \times \vec{a}_3) \cdot \vec{a}_1 \]  

The reciprocal lattice vectors satisfy: 

\[ \vec{a}_i^* \cdot \vec{a}_j = 2\pi \delta_{ij} \]  

Example: Rectangular lattice: 

\[ \vec{a}_1 = a_1 \hat{x} \]
\[ \vec{a}_2 = a_2 \hat{y} \]
\[ \vec{a}_3 = a_3 \hat{z} \]

Then 

\[ \mathcal{N} = (\vec{a}_2 \times \vec{a}_3) \cdot \vec{a}_1 = a_1 a_2 a_3. \]

Now 

\[ \vec{a}_2 \times \vec{a}_3 = a_2 a_3 \hat{y} \times \hat{z} = a_2 a_3 \hat{x} \]
\[ \vec{a}_3 \times \vec{a}_1 = a_1 a_3 \hat{y} \]
\[ \vec{a}_1 \times \vec{a}_2 = a_1 a_2 \hat{z}. \]

Thus 

\[ \vec{a}_1^* = \frac{2\pi}{a_1} \hat{x} \]
\[ \vec{a}_2^* = \frac{2\pi}{a_2} \hat{y} \]
\[ \vec{a}_3^* = \frac{2\pi}{a_3} \hat{z} \]
These vectors are again orthogonal but their magnitudes are inversely proportional to the magnitudes of the corresponding lattice vectors.

Example: fcc lattice: The convenient lattice vectors are:

\[ \hat{a}_1 = \frac{a}{2} (1, 0, \frac{1}{2}) \]
\[ \hat{a}_2 = \frac{a}{2} (0, 1, \frac{1}{2}) \]
\[ \hat{a}_3 = \frac{a}{2} (0, 0, 1) \]

Now \[ \hat{a}_2 \times \hat{a}_3 = \begin{vmatrix} 1 & 0 & \frac{1}{2} \\ 0 & \frac{1}{2} & 0 \\ 0 & 0 & \frac{1}{2} \end{vmatrix} = \frac{a^2}{4} (1, \frac{1}{2}, -\frac{1}{2}) \]

Then \[ \hat{a}_3 \times \hat{a}_1 = \frac{a^2}{4} (\frac{1}{2}, 1, -\frac{1}{2}) \]
\[ \hat{a}_1 \times \hat{a}_2 = \frac{a^2}{4} (\frac{1}{2}, -\frac{1}{2}, 1) \]

Also \[ (\hat{a}_2 \times \hat{a}_3) \cdot \hat{a}_1 = \frac{a^3}{8} \cdot 2 = \frac{a^3}{4} \]

Thus \[ \hat{a}_1^* = \frac{2\pi}{a} (1, \frac{1}{2}, -\frac{1}{2}) \]
\[ \hat{a}_2^* = \frac{2\pi}{a} (-\frac{1}{2}, 1, \frac{1}{2}) \]
\[ \hat{a}_3^* = \frac{2\pi}{a} (\frac{1}{2}, -\frac{1}{2}, 1) \]

Note \[ \hat{a}_1^* + \hat{a}_2^* = \frac{4\pi}{a} (1, 0, 0) \]
\[ \hat{a}_1^* + \hat{a}_3^* = \frac{4\pi}{a} (0, 1, 0) \]
\[ \hat{a}_2^* + \hat{a}_3^* = \frac{4\pi}{a} (0, 0, 1) \]

These vectors give a cubic structure.

The reciprocal lattice vectors are:

The lattice vectors (fcc) and the reciprocal lattice vectors.
The reciprocal lattice consists of all vectors

\[ n_1 \vec{a}_1^* + n_2 \vec{a}_2^* + n_3 \vec{a}_3^* \]

where \( n_1, n_2, n_3 \) are integers. One can see that it generates a lattice in the same way that

\[ m_1 \vec{a}_1 + m_2 \vec{a}_2 + m_3 \vec{a}_3 \]

generate the original lattice.

**Reciprocal lattice and scattering**

The reciprocal lattice is useful in scattering as a method to construct the scattering vectors. So with

\[ \vec{s} = h \vec{a}_1^* + k \vec{a}_2^* + l \vec{a}_3^* \]  \( - (11) \)

We have

\[
\begin{align*}
\vec{s} \cdot \vec{a}_1 &= 2\pi h \\
\vec{s} \cdot \vec{a}_2 &= 2\pi k \\
\vec{s} \cdot \vec{a}_3 &= 2\pi l
\end{align*}
\]  \( - (12) \)

Thus we can construct a large collection of scattering vectors using the reciprocal lattice vectors. In fact one can show that every scattering vector has the form of (11) for some integers \( h, k, l \). This rests on the fact that if \( \vec{a}_1, \vec{a}_2, \vec{a}_3 \) are linearly independent then so are \( \vec{a}_1^*, \vec{a}_2^*, \vec{a}_3^* \). Thus one can express

\[ \vec{s} = s_1 \vec{a}_1^* + s_2 \vec{a}_2^* + s_3 \vec{a}_3^* \]

But

\[
\begin{align*}
\vec{s} \cdot \vec{a}_1 &= 2\pi s_1 = 2\pi h & \implies & s_1 = h \\
\vec{s} \cdot \vec{a}_2 &= 2\pi s_2 = 2\pi k & \implies & s_2 = k \\
\vec{s} \cdot \vec{a}_3 &= 2\pi s_3 = 2\pi l & \implies & s_3 = l \\
\end{align*}
\]

etc...
Every scattering vector is an element of the reciprocal lattice:

\[ \vec{S}_{hkl} = \frac{h}{a_1^*} \hat{a}_1 + \frac{k}{a_2^*} \hat{a}_2 + \frac{l}{a_3^*} \hat{a}_3 \]

For integers \( h, k, l \). So the search for scattering vectors has been replaced by the search for a reciprocal lattice.

Reciprocal lattice vectors + lattice planes

We now show how reciprocal lattice vectors can generate lattice planes. Given a vector \( \vec{S}_{hkl} \), the plane passing through the origin consists of all points \( \vec{r} \) which satisfy \( \vec{r} \cdot \vec{S}_{hkl} = 0 \).

However, our previous method for specifying planes used precisely the vectors of (2) and we showed that \( (hkl) \) are the corresponding Miller indices.

We can determine the distance between adjacent planes: Consider the lattice plane passing through the origin. Suppose that the nearest plane contains a lattice point

\[ \vec{r} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3 \]

Then the distance between these planes is:

\[ \frac{1}{|\vec{S}_{hkl}|} = \frac{2\pi |n_1h + n_2k + n_3l|}{|\vec{S}_{hkl}|} \]
The nearest plane is the one for which \( n_1, n_2, n_3 \) reduce this to a minimum. Again there are two cases.

i) \( h, k, l \) do not have any common factors \( \geq 1 \) \( \Rightarrow \) a number theory result implies that one can find \( n_1, n_2, n_3 \) so that
\[
|n_1 h + n_2 k + n_3 l| = 1.
\]
\( \Rightarrow \) distance between adjacent planes is \( \frac{2\pi}{15hl} \).

ii) The largest factor that \( h, k, l \) contain is \( n \geq 2 \). Then the distance is
\[
\frac{n2\pi}{15hl}.
\]

Thus the distance between adjacent planes is
\[
d_{hkl} = \frac{n2\pi}{15hl}.
\]

- (14)

where \( n \) is the largest integer factor that \( h, k, l \) share.

**Bragg condition.**

Recall that if \( \hat{s}_{hkl} \) defines a plane, one can view scattering as reflection in the perpendicular lattice planes,

\[
\begin{aligned}
|\hat{s}| &= 2k_0\sin\theta \\
&\Rightarrow |\hat{s}_{hkl}| = \frac{4\pi}{\lambda} \sin\theta
\end{aligned}
\]

\[
\Rightarrow \frac{2\pi n}{d_{hkl}} = \frac{4\pi}{\lambda} \sin\theta \Rightarrow n\lambda = 2d_{hkl}\sin\theta
\]

which is exactly the Bragg condition in general.