Lecture 13

Diffraction by a monoatomic lattice with a basis: the geometrical structure factor

So far, we have considered a perfect monoatomic Bravais lattice and diffraction condition based on that. The diffraction condition essentially was that the scattered rays from the atoms of a Bravais lattice cell will interfere constructively. Now, consider we have a non-Bravais lattice, specifically a lattice with a basis. It means, we can construct the lattice by inputting the basis units at each site of a Bravai lattice (we discussed this in Bravais lattice section previously).

Consider the crystal structure that is of a monoatomic lattice with an n-atom basis. For example, BCC lattice is a sc lattice with a basis containing a corner atom and the atom at the center. Another example is the Carbon in a diamond lattice (with 4-atom basis) or Beryllium in a hexagonal closed pack structure. In this case, we have to further analyze the diffraction conditions including the atoms of the

basis. For the n-atom basis, we consider a set of identical scatterer at positions $\vec{d}_1, \vec{d}_2, \ldots, \vec{d}_n$ within the unit cell. The intensity of the radiation in a given Bragg peak will depend on the extent to which the rays scattered from these basis sites interfere with each other. The intensity will be greatest if there is complete constructive interference and vanishing altogether if there is complete destructive interference.

Consider a Bragg peak (that would happen if the basis was just a single atom) associated with a change in the wave-vector $\vec{G} = \vec{k}' - \vec{k}$. Than, according to the derivation of the Laue condition, the phase difference between the rays scattered by basis atoms at $\vec{d}_i$ and $\vec{d}_j$ is given by $\vec{G} \cdot (\vec{d}_i - \vec{d}_j)$. The amplitudes of the two rays will then differ by a factor of $e^{i\vec{G} \cdot (\vec{d}_1 - \vec{d}_2)}$.

To show what it means, consider two waves given by ψ_i and ψ_j at a particular time, and position having the same amplitude and wavelength. We write, $\psi_i = A e^{i\delta_i}$ and $\psi_j = A e^{i\delta_j}$

where ρ_i and ρ_j are the phases of the waves at that time at some particular place.

Now, $\frac{\psi_i}{\psi_j} = e^{i(\rho_i - \rho_j)}$ | $\rho_j - \rho_i$ = phase difference

$$\therefore \psi_j = e^{-i(\rho_j - \rho_i)} \psi_i$$

Hence, the amplitude at a particular time and position differs by a multiplicative factor of e^{it} $e^{i(\rho_j - \rho_i)}$.

Now, $\psi_2 = e^{i(\rho_2 - \rho_1)} \psi_1 = e^{i\vec{G}\cdot(\vec{d}_2 - \vec{d}_1)} \psi_1$

$\psi_3 = e^{i(\rho_3 - \rho_1)} \psi_1 = e^{i\vec{G}\cdot(\vec{d}_3 - \vec{d}_1)} \psi_1$

$\vdots$

$\psi_n = e^{i(\rho_n - \rho_1)} \psi_1 = e^{i\vec{G}\cdot(\vec{d}_n - \vec{d}_1)} \psi_1$

The net ray scattered by the whole set is the sum of individual rays, and will therefore have an amplitude containing the factor,

$$S_G = \sum_{j=1}^{n} e^{i\vec{G}\cdot\vec{d}_j}$$

To see this, we have the superimposed ray

$$\psi = \psi_1 + \psi_2 + \cdots + \psi_n$$

$$= \psi_1 + e^{i\vec{G}\cdot(\vec{d}_2 - \vec{d}_1)}\psi_1 + e^{i\vec{G}\cdot(\vec{d}_3 - \vec{d}_1)}\psi_1 + \cdots$$

$$= \left(1 + \frac{e^{i\vec{G}\cdot\vec{d}_2}}{e^{i\vec{G}\cdot\vec{d}_1}} + \frac{e^{i\vec{G}\cdot\vec{d}_3}}{e^{i\vec{G}\cdot\vec{d}_1}} + \cdots\right)\psi_1$$

$$= \psi_1 e^{-i\vec{G}\cdot\vec{d}_1}\left(e^{i\vec{G}\cdot\vec{d}_1} + e^{i\vec{G}\cdot\vec{d}_2} + \cdots + e^{i\vec{G}\cdot\vec{d}_n}\right)$$

$$\therefore \psi = \psi_1 e^{-i\vec{G}\cdot\vec{d}_1} \sum_{j=1}^{n} e^{i\vec{G}\cdot\vec{d}_j}$$

$$\therefore \psi \propto \sum_{j=1}^{n} e^{i\vec{G}\cdot\vec{d}_j}$$

The quantity S_k is known as the geometrical structure factor, that expresses the extent to which the interference of the waves scattered from the identical atoms within the basis can diminish the intensity of the Bragg peak associated with the reciprocal lattice vector $\vec{G} = \vec{k}' - \vec{k}$. The intensity of the Bragg peak, being proportional to the square of the amplitude, will contain a factor of $|S_G|^2$. There are other sources of G-dependency to the intensity, and hence

the structure factor alone can't be used to predict the absolute intensity of ~~the Bragg peak~~ a Bragg peak. However, in one case when the structure factor can be used with assurance is when it vanishes. This occurs when the atoms in the basis are so arranged that there is complete destructive interference for the $\vec{G}$ in the question.

Applications of structure factor

1. Body centered cubic considered as simple cubic with a basis:

Since BCC is a Bravais lattice, we know that Bragg reflections will occur when the change in wave-vector $\vec{k}$ is a vector of the reciprocal lattice, which is the face centered cubic lattice. Sometimes, it is convenient to regard the BCC lattice as a SC Bravais lattice with primitive vectors $a\hat{x}, a\hat{y}$ and $a\hat{z}$, with a two point basis consisting of $\vec{d}_1 = 0\hat{x} + 0\hat{y} + 0\hat{z}$ and $\vec{d}_2 = \frac{a}{2}(\hat{x}+\hat{y}+\hat{z})$ (which is at the center of the cubic conversional unit cell).

From this point of view, the reciprocal lattice also simple cubic, with a cubic cell of side $\frac{2\pi}{a}$. However, there will be now structure factor associated with each Bragg reflection. Here,

$$S_k = \sum_{j=1}^{2} e^{i \vec{G} \cdot \vec{d}_j} = e^{i \vec{G} \cdot \vec{d}_1} + e^{i \vec{G} \cdot \vec{d}_2}$$

$$= e^{i \frac{2\pi}{a} (n_1 \hat{x} + n_2 \hat{y} + n_3 \hat{z}) \cdot 0} + e^{i \frac{2\pi}{a} (n_1 \hat{x} + n_2 \hat{y} + n_3 \hat{z}) \cdot \frac{a}{2} (\hat{x} + \hat{y} + \hat{z})}$$

$$= 1 + e^{i\pi (n_1 + n_2 + n_3)}$$

$$= 1 + (-1)^{n_1 + n_2 + n_3}$$

$$\therefore S_k = \begin{cases} 2 ; & n_1 + n_2 + n_3 = \text{even} \\ 0 ; & n_1 + n_2 + n_3 = \text{odd} \end{cases}$$

Thus, the points in the simple cubic reciprocal lattice whose sum of coordinates w.r.t. the cubic primitive vectors are odd, will have no Bragg reflection associated with them, and others will survive. Consider the figure here, that shows the reciprocal lattice. The white circles represents lattice sites for which Bragg reflection vanishes. The surviving ones, creates an fcc reciprocal lattice with ~~cubic~~ cube edge length $\frac{4\pi}{a}$, which is exactly one would expect, since

reciprocal of the BCC lattice with cube edge a is an fcc lattice with cube edge $\frac{4\pi}{a}$. So, the proper Bragg reflection prediction is made using the structure factor.

2. Monoatomic diamond lattice: The monoatomic diamond lattice (Carbon, silicon, germanium etc.) is not a Bravais lattice and must be described as a lattice with a basis. The underlying Bravais lattice is fcc, with a two-atom basis at $\vec{d}_1 = 0\hat{x} + 0\hat{y} + 0\hat{z}$ and $\vec{d}_2 = \frac{a}{4}(\hat{x}+\hat{y}+\hat{z})$, where $\hat{x}$, $\hat{y}$ and $\hat{z}$ are along the cubic axes and a is the side of the unit cell. The reciprocal lattice is a bcc lattice with cube edge $\frac{4\pi}{a}$. Considering the primitive vectors (for a bcc) in reciprocal space, $\vec{b}_1 = \frac{2\pi}{a}(\hat{y}+\hat{z}-\hat{x})$, $\vec{b}_2 = \frac{2\pi}{a}(\hat{z}+\hat{x}-\hat{y})$ and $\vec{b}_3 = \frac{2\pi}{a}(\hat{x}+\hat{y}-\hat{z})$, then the structure factor,

$$S_K = e^{i\vec{K}\cdot(0\hat{x}+0\hat{y}+\hat{z})} + e^{i\vec{K}\cdot\frac{a}{4}(\hat{x}+\hat{y}+\hat{z})}$$

$$= 1 + e^{i(n_1\vec{b}_1+n_2\vec{b}_2+n_3\vec{b}_3)\cdot\frac{a}{4}(\hat{x}+\hat{y}+\hat{z})}$$

$$= 1 + e^{i\frac{\pi}{2}(n_1+n_2+n_3)}$$

$$\therefore S_K = \begin{cases} 2, & \text{if } n_1+n_2+n_3 = \text{twice an even num} \\ 1\pm i, & \text{if } n_1+n_2+n_3 = \text{odd} \\ 0, & \text{if } n_1+n_2+n_3 = \text{twice an odd number} \end{cases}$$

To interpret the result of Σn_i geometrically, if we substitute the primitive vectors $\vec{b}_i$ in the general reciprocal lattice vector,

$$\vec{K} = n_1 \cdot \frac{2\pi}{a}(\hat{y}+\hat{z}-\hat{x}) + n_2 \frac{2\pi}{a}(\hat{z}+\hat{x}-\hat{y}) + n_3 \frac{2\pi}{a}(\hat{x}+\hat{y}-\hat{z})$$

$$\therefore \vec{K} = \frac{4\pi}{a}(\nu_1 \hat{x} + \nu_2 \hat{y} + \nu_3 \hat{z}) \quad \text{——(i)}$$

with $\nu_j = \frac{1}{2}(n_1+n_2+n_3) - n_j$; $\sum_{j=1}^{3} \nu_j = \frac{1}{2}(n_1+n_2+n_3)$ ——(ii)

We know that, the reciprocal to the fcc lattice with a cubic cell of side a is a bcc lattice with side $\frac{4\pi}{a}$. Let us consider the bcc lattice being composed of two sc lattices of side $\frac{4\pi}{a}$. The first sc one contains the origin ($\vec{K}=\vec{0}$). Since it's a simple cubic lattice, according to (i), the values of ν_i's them must be integers. For example, for the origin, $\vec{K} = \frac{4\pi}{a}(0\hat{x}+0\hat{y}+0\hat{z})$, for one of the nearest neighbours, $\vec{K} = \frac{4\pi}{a}(\hat{x}+0\hat{y}+0\hat{z})$, and so on so forth. Since ν_i's are all integers, according to (ii), $n_1+n_2+n_3$ must be even. The

second one, ☨ containing the body-centered point $\frac{4\pi}{a} \cdot \frac{1}{2}(\hat{x}+\hat{y}+\hat{z})$ as a corner point of the sc lattice, must have all V_i's to be integers $+\frac{1}{2}$ according to (i) and must therefore be given by $n_1+n_2+n_3$ odd.

So, the points with structure factor $1 \pm i$ are those in the simple cubic sublattice containing the body centered points. Those with $S_G = 2$ or $S_k = 0$ are in the simple cubic sublattice containing the origin, where $\sum V_i$ is even when $S_G = 2$ and $\sum V_i$ = odd when $S_G = 0$. We again remove the points with zero structure factor, and the resulting reciprocal lattice is as shown in the figure.

Diffraction by a polyatomic crystal

If the atoms in the basis are not identical, the structure factor assumes the form

$$S_G = \sum_{j=1}^{n} f_j(\vec{G})\, e^{i\vec{G}\cdot\vec{d}_j}$$

where f_j is known as the atomic form factor.

which is completely determined by the internal structure of the ion that occupies position $\vec{d}_j$ in the basis. Identical ions have identical structure factor, and so, for monoatomic crystals,

$$S_G = \sum_{j=1}^{n} f\, e^{i\vec{G}\cdot\vec{d}_j}$$

In elementary treatments of the atomic form factor associated with a Bragg reflection given by the reciprocal lattice vector $\vec{G}$ is taken to be proportional to the Fourier transform of the electronic charge distribution of the corresponding atom/ion, and is defined as -

$$f_j(\vec{G}) = -\frac{1}{e}\int d^3r\, e^{i\vec{G}\cdot\vec{r}}\, \rho_j(\vec{r})$$