

# Lecture 3 Wave Diffraction and the Reciprocal Lattice

Simon: Chapter 14 (pp141-158)

*See also Kittel Chapter 2 (pp 25-30)*

## Diffraction of waves by crystals

The structure of crystals is extensively studied by the diffraction of waves (or particles). Photons, neutrons and electrons are used. Each of these have different wavelength ranges allowing interaction with a broad range of crystal structures. (Kittel Figure 2.1 page 24 shows full range on graph). Wavelength ranges from 0.01 nm -10 nm can be used to probe crystals.

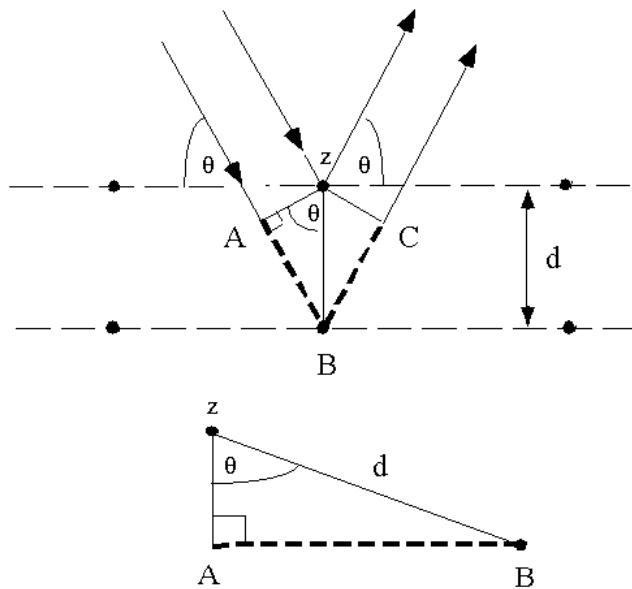
The interaction of light with solids is described in optics as diffraction. At the wavelength of visible light, 500 nm for green, waves are scattered elastically by a solid. When the wavelength of the incident radiation is similar to the spacing between the atoms (lattice constant) interactions lead to diffracted beams in specific directions.

William Lawrence Bragg developed a very elegant and simple law: **Bragg's law of x-ray diffraction** in 1912. He was awarded Nobel Prize in 1915 at the age of 25 (shared with his father W H Bragg).

The concept behind Bragg's law is that incident waves undergo specular reflection from parallel planes of atoms in crystals with each plane reflecting a small proportion of the incident beam. (Scattering is from lattice – electrons as symmetric particles with Coulomb field scatter in all directions)

One example of specular reflection is a partly silvered mirror. The angle of incidence is equal to the angle of reflection. The diffracted x-ray beam occurs when the partial reflections from each plane add up constructively.

Consideration of the geometry of parallel planes:

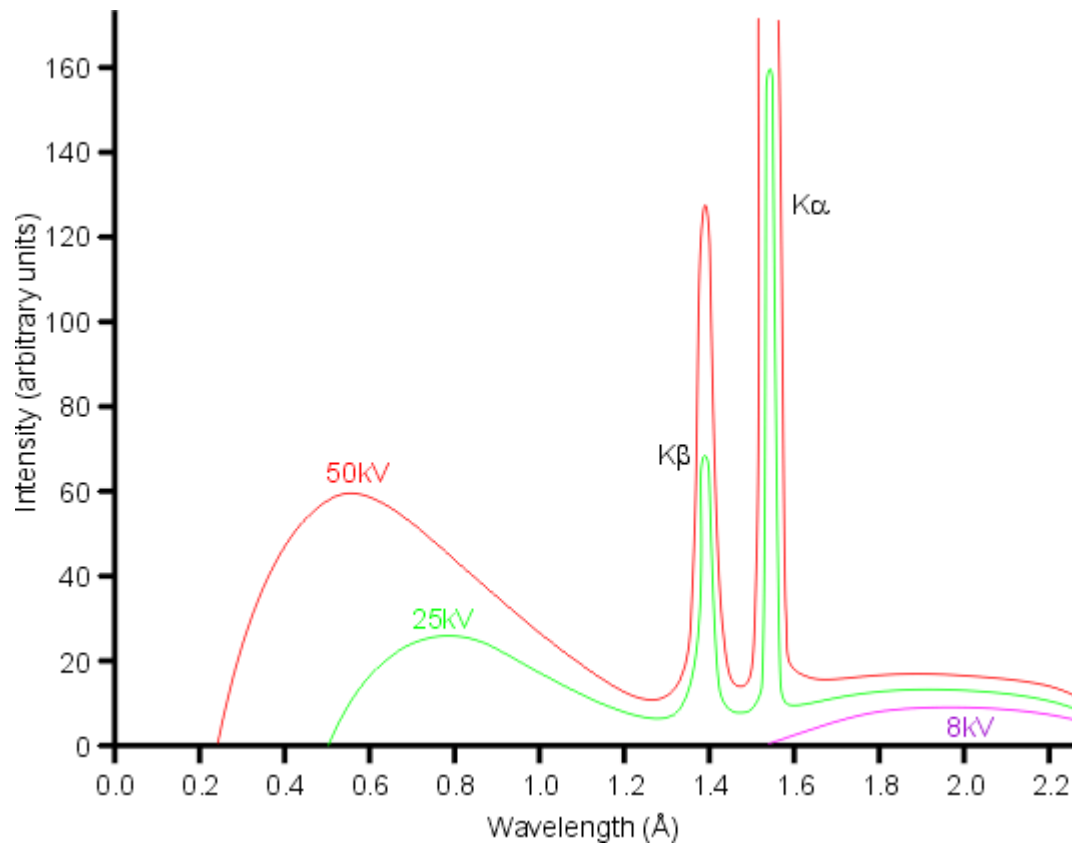


The planes are spaced  $d$  apart. The path length difference for x-rays reflected from adjacent planes (ABC in the diagram above) is  $2d \sin \theta$ . Constructive interference occurs when this path difference is an integral number of wavelengths  $\lambda$  which gives:

$$2d \sin \theta = n \lambda$$

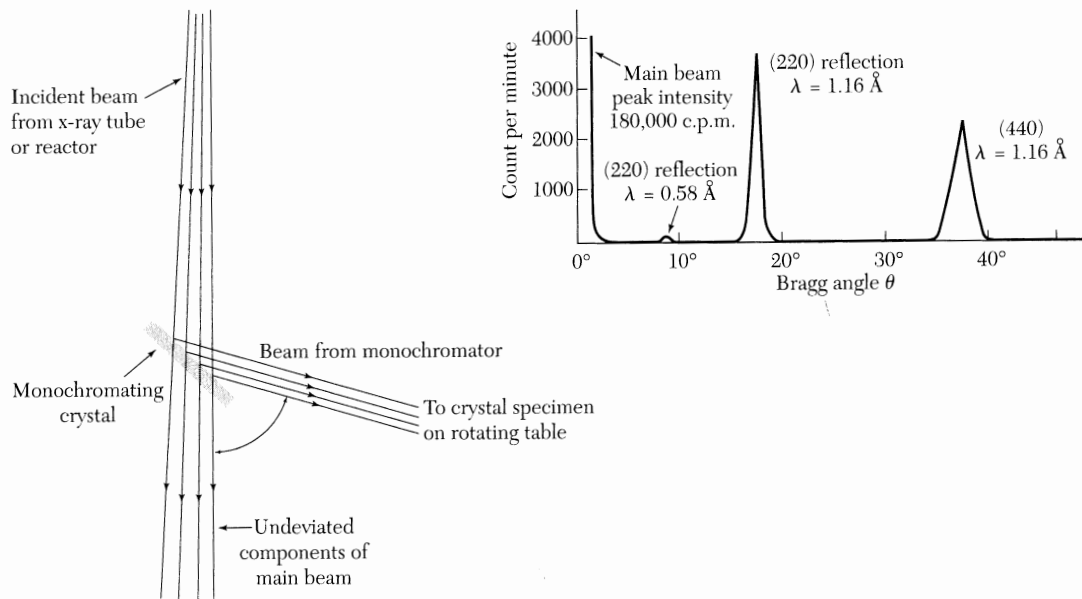
This is Bragg's law. For the law to be valid  $\lambda \leq 2d$ . ( $n$  is order of diffraction, usually only order 1 is explicitly considered).

An x-ray generator consists of a beam of high energy electrons from a heated filament fired at a metal target. The x-rays originate from transitions between the K, L and M orbitals – those with principal quantum numbers 1,2,3. The process is about 1% efficient. A common x-ray generator target is copper. The spectra from Cu is shown in the figure.

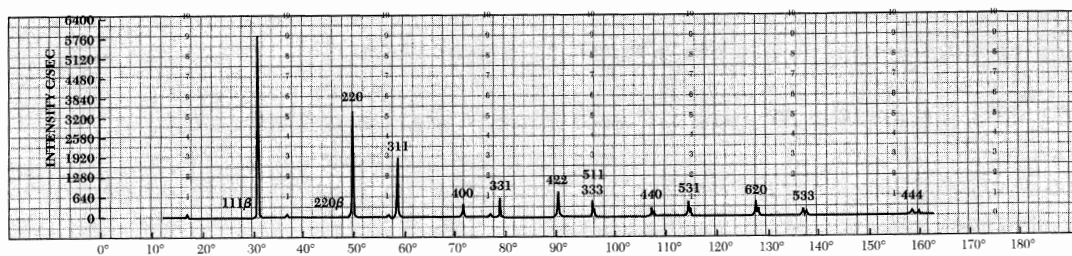


The most intense line is the Cu-K $\alpha$  line (which is a doublet). The centre wavelength of the doublet (weighted intensity 1:2) is 0.15418 nm.

It is observed that each plane of atoms reflects  $10^{-3}$ - $10^{-5}$  of the incident radiation so the x-ray diffraction pattern is the result of  $10^3$ - $10^5$  atomic planes which typically occurs 1-100  $\mu\text{m}$  of the surface.



**Figure 3** Sketch of a monochromator which by Bragg reflection selects a narrow spectrum of x-ray or neutron wavelengths from a broad spectrum incident beam. The upper part of the figure shows the analysis (obtained by reflection from a second crystal) of the purity of a 1.16 Å beam of neutrons from a calcium fluoride crystal monochromator. (After G. Bacon.)



**Figure 4** X-ray diffractometer recording of powdered silicon, showing a counter recording of the diffracted beams. (Courtesy of W. Parrish.)

Bragg's Law is a consequence of the **lattice** and does not take account of the basis. It will be shown later that the composition of the basis determines the intensity of the different diffraction peaks (structure factor).

Bragg's law is a very simple condition arising from the geometric properties of a crystal *lattice*.

Bragg's law is a direct consequence of the periodic nature of a crystal lattice. A more detailed analysis of periodic structures can be undertaken using **Fourier Analysis**.

To illustrate this, we begin with considering a crystal lattice. We know that the crystal lattice is invariant under any translation **T** of the form:

$$\mathbf{T} = u_1\mathbf{a}_1 + u_2\mathbf{a}_2 + u_3\mathbf{a}_3 \text{ where } u_i \text{ are integers and } \mathbf{a}_i \text{ are the crystal axes.}$$

We also know that because of this any local physical property of the crystal will also be invariant under **T**.

Many properties of crystal depend on the electron density  $n(\mathbf{r})$ . We know that:

$$n(\mathbf{r} + \mathbf{T}) = n(\mathbf{r})$$

This tells us that the local physical environment at positions  $\mathbf{r}$  and  $\mathbf{r} + \mathbf{T}$  are the same.

Fourier analysis assumes that a function can be expressed as a linear combination of sin and cos functions. (This is a direct consequence of the periodicity of the crystal lattice).

We begin by looking at the electron density  $n$  in one dimension  $x$ . We assume that the periodicity in the  $x$  direction (the lattice constant) is  $a$ :

$$n(x) = n_0 + \sum_{p>0} \left[ C_p \cos\left(\frac{2\pi px}{a}\right) + C_s \sin\left(\frac{2\pi px}{a}\right) \right]$$

where  $p$  are positive integers,  $C_p$  and  $C_s$  are real constants called the Fourier coefficients of the expansion.

The factor  $2\pi/a$  in the arguments of the sin and cos function is very important. This ensures that the function  $n(x)$  has the period of  $a$ .

See equation (4) page 27 of Kittel. It can be shown that  $n(x + a) = n(x)$ .

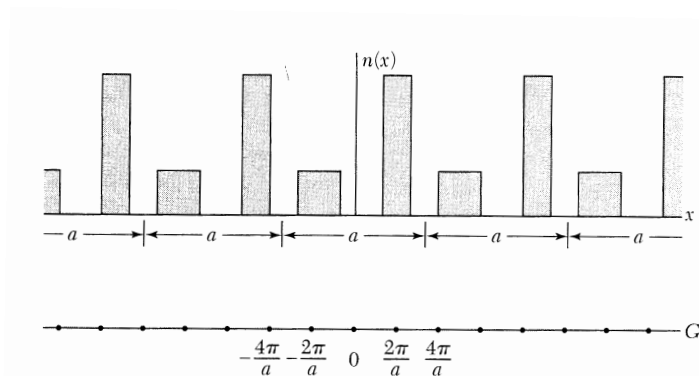
In terms of sin and cos functions this is equivalent to adding  $360^\circ$  or  $2\pi$  to the argument. The result of the function is left unchanged.

The arguments of the sin and cos functions are called the **reciprocal lattice points**. They represent the frequency components of the sin and cos functions which, when combined together, reconstruct the lattice. The presence of the  $2\pi/a$  factor requires these functions to have the periodicity of the lattice.

Let's pause to think about **units** to help clarify some nomenclature.

We know that sin and cos functions are trigonometric ratios and don't have units. Angles are expressed in degrees or radians and also don't have units – they do not represent a physical quantity.

The quantity  $2\pi p/a$  is the basis of the series over which the summation is performed. The allowed values are evenly spaced and separated by an amount  $2\pi/a$ .



**Figure 5** A periodic function  $n(x)$  of period  $a$ , and the terms  $2\pi p/a$  that may appear in the Fourier transform  $n(x) = \sum n_p \exp(i2\pi p x/a)$ .

The allowed points form what is called the **reciprocal lattice points**. They have the dimensions of inverse length (or frequency in length). These points tell us the allowed terms in the Fourier series above. Only terms which are consistent with the periodicity of the crystal are allowed ( $a$  in real space and  $2\pi/a$  in reciprocal space). Points which fall in between in reciprocal space are not allowed in the Fourier series. The series of *reciprocal lattice points* themselves make up their own structure in reciprocal space. Knowing all the Fourier components (length frequency components) allows the crystal to be reconstructed from this frequency or Fourier information.

The reciprocal relationship between the lattice and reciprocal lattice is very important and is a direct consequence of the periodic nature of the lattice.

A *point* in reciprocal space represents a single frequency in real space which extends throughout the entire crystal. (This can be considered equivalent to a family of planes denoted by a single set of Miller Indices  $(h \ k \ l)$ )

Thinking back to Lecture 2 we note that crystal planes are defined by the *reciprocal* of the lattice vectors  $\mathbf{a}_{123}$

**Reciprocals** are important for a number of reasons:

1. By taking reciprocals we bring all the planes inside a single unit cell. (Even very high order planes can be made to intersect the unit cell).
2. The unit cell is used to generate the crystal and therefore the unit cell is representative of the whole crystal. The properties of the unit cell will be the properties of the crystal.
3. The unit cell is analogous to the molecule in chemistry – it is the fundamental building block. Every equation which applies to the unit cell applies to the whole crystal.

The use of reciprocals is key to crystal structure and the properties of crystals. We will return to reciprocals again when we look at mechanisms for probing and describing the properties of crystals. The concept of **reciprocal space** is fundamental to condensed matter physics.

Although reciprocal vectors have units of inverse length – you should think of them as simply coordinates which describe the properties of a crystal plane (rather than an

individual atom). We will see later in the course that many physical properties of particles in crystals can be related to the position in reciprocal space or wavevector.

The equation above can be written in the complex exponential form which combines the sin and cos functions:

$$n(x) = \sum_p n_p \exp(i2\pi px/a)$$

In this case the sum is over all integers  $p$  +ve, -ve and zero. The coefficients  $n_p$  are now complex numbers.

The requirement that  $n(x)$  is a real function puts a constraint on the coefficients  $n_p$  such that  $n_{-p}^* = n_p$  where the  $*$  denotes the complex conjugate.

(complex exponential - see discussion in Kittel page 28 (equations 6-8) for full details).

It is straightforward to extend the Fourier representation into 3 dimensions where  $x$  is replaced by a vector  $\mathbf{r}$ .

$$n(\mathbf{r}) = \sum_{\mathbf{G}} n_{\mathbf{G}} \exp(i\mathbf{G} \cdot \mathbf{r})$$

We now have a periodic function in three dimensions  $n(\mathbf{r})$ . There exists a set of vectors  $\mathbf{G}$  that mean that  $n(\mathbf{r})$  is invariant under all crystal translations  $\mathbf{T}$ .

Kittel develops a relationship between the volume of the crystal unit cell and the vectors  $\mathbf{G}$ .

## Reciprocal Lattice Vectors

We now introduce a key concept in describing crystals the **reciprocal lattice vectors**. These vectors provide a powerful mathematical representation of crystals which enables a theoretical determination of many of the physical properties of crystals. The concept of reciprocal lattice vectors is possible because of the highly periodic nature of crystals.

One of the end points of this approach is the determination of the function  $n(\mathbf{r})$  which is a function describing the electron density (or number density) in a crystal as a function of position vector  $\mathbf{r}$ .

To achieve this we need to identify the vectors  $\mathbf{G}$  of the frequency (or Fourier) sum above.

To do this we construct the vectors of the axes of the *reciprocal lattice*.

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3} \quad \mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3} \quad \mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3}$$

Note that the vectors have units of inverse length ( $\text{length}^2 / \text{length}^3$ ).

The factors  $2\pi$  reflect the periodic nature as described above.

As the vectors  $\mathbf{a}_{1,2,3}$  are the primitive vectors of the crystal lattice, so the vectors  $\mathbf{b}_{1,2,3}$  are the vectors of the *reciprocal lattice*. Each vector defined by the equation above is orthogonal to two axis vectors of the crystal lattice (this is a consequence of the vector cross products). This means that:

$$\mathbf{a}_j \cdot \mathbf{b}_i = 2\pi\delta_{ij}$$

where  $\delta_{ij}$  is the kronecker delta function = 1 when  $i = j$  and = 0 when  $i \neq j$ .

The reciprocal lattice is constructed from the  $\mathbf{b}$  vectors in the same way as for the crystal lattice:

$$\mathbf{G} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$$

Where (as before)  $h, k, l$  are integers.  $\mathbf{G}$  is the **reciprocal lattice vector**.

If the vectors  $\mathbf{G}$  in the Fourier expansion for  $n(\mathbf{r})$  are equated with the reciprocal lattice vectors, this results in the Fourier series expression for the electron density  $n(\mathbf{r})$  having the desired invariance under any crystal translation  $\mathbf{T}$ .

If we have  $\mathbf{T} = u_1\mathbf{a}_1 + u_2\mathbf{a}_2 + u_3\mathbf{a}_3$  then:

$$n(\mathbf{r} + \mathbf{T}) = \sum_{\mathbf{G}} n_{\mathbf{G}} \exp(i\mathbf{G} \cdot \mathbf{r}) \exp(i\mathbf{G} \cdot \mathbf{T})$$

but we know that:

$$\begin{aligned} \exp(i\mathbf{G} \cdot \mathbf{T}) &= \exp[i(h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3) \cdot (u_1\mathbf{a}_1 + u_2\mathbf{a}_2 + u_3\mathbf{a}_3)] \\ &= \exp[i2\pi(hu_1 + ku_2 + lu_3)] = 1 \end{aligned}$$

The exponential is  $2\pi i$  times an integer.

This confirms the desired invariance  $n(\mathbf{r} + \mathbf{T}) = n(\mathbf{r})$ .

Using this formalism means that every crystal has a **crystal lattice** and a **reciprocal lattice**.

At the moment the *reciprocal lattice* is simply a mathematical construct that satisfies the condition that it is also invariant under a lattice translation  $\mathbf{T}$ . However, the reciprocal lattice is also a powerful tool for predicting many of the properties of crystal lattices. We have a function  $n(\mathbf{r})$  which describes the electron density as a function of position in the lattice.



The reciprocal lattice is equivalent to the frequency (or Fourier) components of this function. Each reciprocal lattice point (described by a reciprocal lattice vector) is equivalent to well define period in the crystal lattice equivalent to a *family* of planes described by a set of Miller indices. The family of planes is infinite.

This leads to the important analogy:

*A reciprocal lattice point is equivalent to a single family of planes.*

We have previously described the scattering of x-rays from a crystal lattice as equivalent to specular reflection from planes of atoms (when the Bragg condition is satisfied). (Remember the partially silvered mirror). We know that a particular plane in the crystal (described by the  $hkl$  Miller indices) will have a well-defined periodicity which corresponds to a defined point in reciprocal space. Therefore, when x-rays scatter of a crystal plane they can also be considered to scatter off a **reciprocal lattice point in reciprocal space**.

An x-ray diffraction pattern is a map of the reciprocal lattice of the crystal. Having a map of the reciprocal lattice allows a reconstruction of the real crystal lattice. Determining maps of reciprocal lattices by x-rays is much easier than determining real space maps of crystal lattices (which would require extremely high power microscopes).

Remember units: lattice vectors in direct (or real) space have units of length, lattice vectors in reciprocal space have units of inverse length. The reciprocal lattice exists in Fourier space. Vectors in reciprocal space (or Fourier space) are called **wavevectors**.