

Lecture notes

X-ray diffraction by crystals

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These notes are based on a series of lectures given to graduate physics students at YCM, University of Mysore, as part of the PHYS403 specialisation course in solid-state physics.

Please e-mail hello@vhbelvadi.com with your thoughts or suggestions, or if you spot any errors. These notes are – and will probably always remain – a work in progress. They may be updated and, if they are, the latest version of this document will always be available for download at <http://vhbelvadi.com/notes/> for anybody interested in it.

A note on references: Footnotes are marked by superscript numbers ^x, equations by parentheses (x) and references to the appendix by square brackets [x].

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0 The basics

Crystals are an important part of solid-state physics given that they describe quite a large class of solids. Understanding the structure of crystals, in turn, is one of the biggest steps in understanding the energies associated with them and the manner in which they interact with their surroundings and with other crystals, and also in understanding how their own component atoms and molecules interact with each other.

This is §0 since our discussion really starts with reciprocal lattices in §1, but any text on X-ray diffraction would feel incomplete without at least a brief mention of the fundamental ideas behind studies of crystals.

0.1 Definitions

Although our intention now is to understand how X-rays may be used to study crystals, we may, for completeness, we start with some basic definitions related to crystals in general:

Crystal A homogeneous solid that has an ordered (periodic) atomic arrangement in three dimensions and is bounded by plane faces.

Reference/Crystallographic axes The three coördinate axes used to describe lattice points in a crystal (and hence the structure of a crystal) and chosen based on various crystal parameters such as lines of symmetry or crystal faces. These axes may or may not be mutually perpendicular.

Interaxial angles The angles between the three crystallographic axes, represented by α , β and γ , such that the angles are formed on a plane perpendicular to the X , Y and Z axes respectively.

Lattice A regular, infinite arrangement of points in n dimensions (but especially in three) in which every point has the same environment as any other point.

Unit cell The smallest repetitive arrangement of points that contains the entire symmetry of a crystal and that can be translated in n dimensions to form an n dimensional lattice.

Primitive cell The least voluminous segment of a crystal that, by translation can be used to build up the entire crystal¹.

¹A primitive cell is not to be confused with a unit cell. Since the latter must contain information about the symmetry of the crystal, it need not always be the smallest possible segment from which the crystal can be built. The primitive cell is always, by definition, the smallest possible segment.

0.2 Real lattice, Miller index and Miller plane

The points making up a lattice, much like any point objects in physics, are defined using a coördinate system. In this case, the system is defined with respect to the crystal itself (see *crystallographic axes* above). Thanks to its homogeneity, any lattice point may be chosen as the origin. From that point, a **lattice vector**, \mathbf{r} , can be drawn to any other point and can be described using the vectors defining a primitive cell (called the **primitive vectors**) as follows:

$$\mathbf{r} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c} \quad (1)$$

The line described simply as $[u\ v\ w]$ then refers to all the lattice points lying on the lattice vector \mathbf{r} . These are also the Miller indices when given in terms of the unit cell distance: e.g. in a cubic lattice, going one unit cell length in the \mathbf{a} direction, half a unit cell length in the \mathbf{b} direction and one unit cell length in the $-\mathbf{c}$ direction gives us 1, $1/2$, -1 times the unit cell length. This is written as a Miller index in *square brackets*, with negatives denoted by a bar, as $[2\ \bar{1}\ 2]$.

Miller planes are likewise written in terms of the reciprocals of their x , y and z intercepts. A plane that meets the x axis at half the unit cell length and the y axis at the intercept -1 , and runs parallel to the z axis (i.e. meets it at ∞) is described by $\frac{1}{1/2}$, $\frac{1}{-1}$, $\frac{1}{\infty}$ and simplified (to avoid fractions) in *parentheses* as $(2\ \bar{1}\ 0)$.

The notation used to represent Miller indices and planes are $[h\ k\ l]$ and $(h\ k\ l)$ respectively. These also represent entire families of lines or planes which are formed as multiples of these indices. Since these are multiples of the unit cell distance, d , themselves, the general notation would be $d(h\ k\ l)$.

0.3 Bragg and Laue equations

Bragg's law, first proposed by William Lawrence Bragg and William Henry Bragg, establishes an extremely important relationship between incident rays and the structure of a lattice, and therefore plays an especially important role in experimental physics as far as crystals and diffraction are concerned. Since the law itself is outside the scope of our discussion, we will only mention it:

$$n\lambda = 2d \sin \theta \quad (2)$$

where $n\lambda$ is the integral multiple of the wavelength, λ , of an incident ray that is diffracted by a crystal at an angle θ , and d is the lattice spacing of that crystal. Knowing the incident waves then, (2) helps us calculate the lattice spacing by simply measuring the angle of diffraction. Conversely, using a known crystal, Bragg's law helps us calculate the wavelength of an incident electromagnetic ray.

A more generalised formulation of Bragg's law gives a set of equations known as the Laue equations, after Max von Laue. In a crystal diffraction setup, if \mathbf{k}_i is the wave vector of the incident beam and \mathbf{k}_o is that of the diffracted beam, the difference $\mathbf{k}_o - \mathbf{k}_i = \Delta\mathbf{k}$ is known as the scattering vector (and will be described in

greater detail in later sections).

As in (1), if \mathbf{a} , \mathbf{b} and \mathbf{c} are the primitive vectors of our real lattice, the Laue equations describe their relationship with h , k and l , their corresponding reciprocal indices (described in detail in §1) as,

$$\mathbf{a} \cdot \Delta \mathbf{k} = 2\pi h \quad \mathbf{b} \cdot \Delta \mathbf{k} = 2\pi k \quad \mathbf{c} \cdot \Delta \mathbf{k} = 2\pi l \quad (3)$$

Bragg's law and the three Laue equations are actually equivalent. We will see how this comes about later in our discussion of Ewald's construction.

1 Reciprocal lattice

We have seen in (1) how the position of any point on a lattice can be defined by a lattice vector in terms of the unit cell vectors of that lattice. In an X-ray diffraction experiment, the pattern of diffraction obtained is often *not* simply the real lattice but an altogether different pattern with a reciprocal relationship (see §??) to the real lattice. Further, whereas a real lattice is often three-dimensional, its reciprocal lattice is a pattern that gets projected onto a two-dimensional screen. This is like a shadow on a wall: although an object is in three dimensions, its shadow is in two.

The reciprocal lattice exists in reciprocal space (or \mathbf{k} -space) as a result of it being the Fourier transform (FT) of real lattice vectors. For a real vector, \mathbf{a} , its FT is represented as \mathbf{a}^* . What \mathbf{a}^* is, mathematically, will be discussed in §??. For now, if we agree to represent the reciprocal vector, corresponding to some real vector, using an asterisk (*), we may write $\Delta \mathbf{k}$ in terms of reciprocal lattice vectors as

$$\Delta \mathbf{k} = \chi(n_1 \mathbf{a}^* + n_2 \mathbf{b}^* + n_3 \mathbf{c}^*)$$

using some n_1 , n_2 and n_3 that are yet to be determined. We can substitute the above equation into (3) to get

$$\mathbf{a} \cdot \chi(n_1 \mathbf{a}^* + n_2 \mathbf{b}^* + n_3 \mathbf{c}^*) = 2\pi h$$

and likewise for \mathbf{b} and \mathbf{c} , both of which we will not define explicitly henceforth unless they do not equate exactly as \mathbf{a} does. Therefore,

$$\chi(n_1 \mathbf{a}^* \cdot \mathbf{a} + n_2 \mathbf{b}^* \cdot \mathbf{a} + n_3 \mathbf{c}^* \cdot \mathbf{a}) = 2\pi h$$

and, if $\chi = 2\pi$, we have our three equations as

$$n_1 \mathbf{a}^* \cdot \mathbf{a} + n_2 \mathbf{b}^* \cdot \mathbf{a} + n_3 \mathbf{c}^* \cdot \mathbf{a} = h$$

and likewise for k and l too. Choosing $i^* \cdot j = \delta_{ij}$ we realise that $n_1 = h$, $n_2 = k$ and $n_3 = l$. Therefore,

$$\Delta \mathbf{k} = 2\pi(h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*)$$

is the scattering vector in terms of the reciprocal lattice vectors.

Our choice of $i^* \cdot j = \delta_{ij}$ means that, in the above equation, \mathbf{a}^* is perpendicular to \mathbf{b} and \mathbf{c} and we can write it in terms of some scaling factor (scalar), ξ , as $\mathbf{a}^* = \xi(\mathbf{b} \times \mathbf{c})$. This equation is, of course, cyclic².

²Along the same lines, \mathbf{b}^* and \mathbf{c}^* are perpendicular to \mathbf{a} , \mathbf{c} and \mathbf{a} , \mathbf{b} respectively.

Therefore, $\mathbf{a}^* \cdot \mathbf{a} = 1$ implies that $\mathbf{a}^* \cdot \mathbf{a} = \xi(\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}) = 1$, or, $\xi = (\mathbf{a} \cdot \mathbf{b} \times \mathbf{c})^{-1}$ giving us

$$\mathbf{a}^* = \xi(\mathbf{b} \times \mathbf{c}) \Rightarrow \boxed{\mathbf{a}^* = \frac{(\mathbf{b} \times \mathbf{c})}{(\mathbf{a} \cdot \mathbf{b} \times \mathbf{c})}} \quad (4)$$

This equation gives the relationship between a real lattice primitive vector, \mathbf{a} , and its corresponding reciprocal lattice primitive vector, \mathbf{a}^* , and their relationship is clearly reciprocal in nature.

Further, for any $\Delta \mathbf{k} = 2\pi \mathbf{G}$, the term $\mathbf{G} \equiv \mathbf{G}_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$ is known as the **reciprocal lattice vector**. This vector has two important properties:

1. \mathbf{G}_{hkl} is perpendicular to the real lattice vector.
2. The reciprocal lattice vector has its lattice spacing as the reciprocal of that of the real lattice, i.e. $|\mathbf{G}_{hkl}| = 1/d_{hkl}$

2 Fourier transforms

Fourier transforms (FT) play an extremely important role in studying crystals through diffraction. They are a powerful mathematical tool used to understand XRD patterns and before we discuss how diffraction itself occurs, it would help to overview Fourier Transforms purely from a mathematical perspective. This entire section would be dedicated to that.

2.1 Understanding integrals

Integration is a particular operation performed on a function of one or more variables that yields another function of one of those variables (called an indefinite integral) or a number (called a definite integral) or a combination of the two.

Mathematically,

$$\begin{aligned} \int f(x) dx &= g(x) & \int f(x, y) dx &= g(x, y) \\ \int_a^b f(x) dx &= \text{number} & \int_a^b f(x, y) dx &= h(y) \end{aligned}$$

We will focus on integrals containing the term $e^{i\mathbf{k} \cdot \mathbf{r}}$ (or e^{ikx} in case of a single dimension) for reasons that will become clear as we go: primarily, integrals containing this function are what we will come across throughout our study of XRD. Graphically, e^{ikx} looks like fig. 1. As before, $k = 2\pi/\lambda$ is the wave vector.

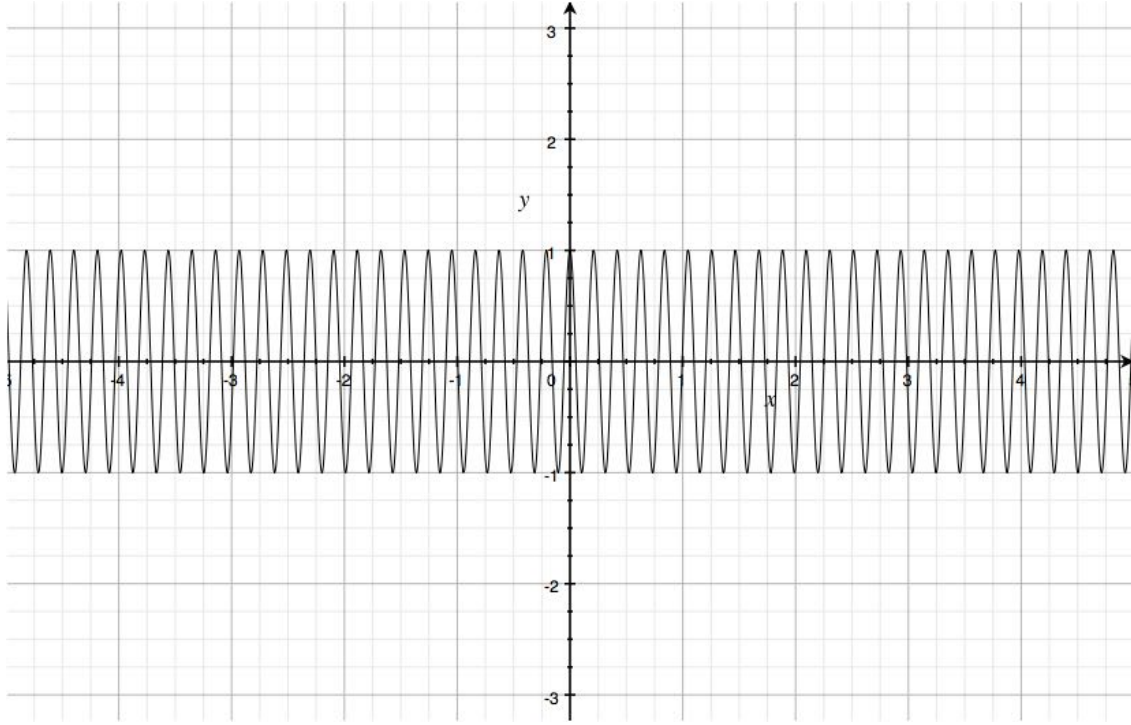


Figure 1: A graph of e^{ikx} with $k = 30$ to exaggerate the compressed shape.

The figure explains itself fairly well. We have

$$e^{ikx} = \cos kx + i \sin kx = \cos \frac{2\pi x}{\lambda} + i \sin \frac{2\pi x}{\lambda}$$

which has limits ± 1 thanks to the sine and cosine functions, and goes to zero when $kx = (2n - 1)\pi/2$, that is, kx is an odd multiple of $\pi/2$. Also, the function has maxima and minima at $kx = 0$ or $\pm n\pi$, or, since $k = 2\pi/\lambda$, the maxima and minima occur at $x = 0$ or \pm integral or half-integral multiples of λ .

2.2 Multiplying two functions

Suppose we now had to multiply two functions, e^{ikx} and some $f(x)$, shown in fig. 2, these are the steps we follow. (For more mathematical steps consult [A1].)

1. Draw the graph of $f(x)$
2. Mirror $f(x)$ about the x-axis to obtain a graph of $-f(x)$
3. Use this as an envelope within which $\pm f(x)$ values (as calculated using $x = 0, \lambda, n\lambda/2$) are plotted.

Fig. 2 also shows such an envelope besides the final graph which shows the product of $f(x)$ and e^{ikx} .

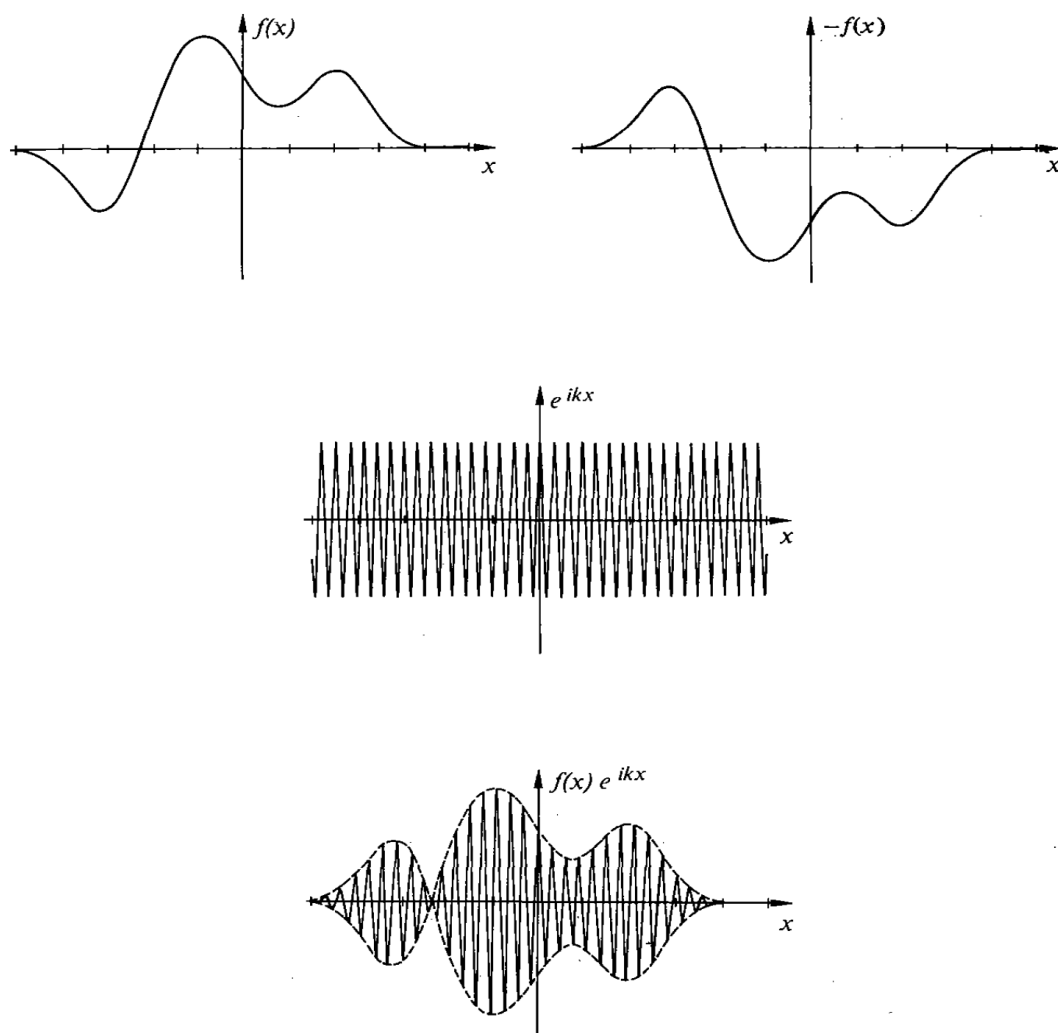


Figure 2: Steps to multiply e^{ikx} and some $f(x)$. Figure borrowed from [B2].

2.3 Fourier transforms

An important equation in physics, and a particularly important equation in discussions of XRD, happens to be the wave equation which contains a term of the form,

$$\int_{-\infty}^{\infty} f(x)e^{ikx} dx$$

and, as we saw in §2.1, the integral of a function of two variables, x and k , over dx , is a function of the other variable, k . Therefore,

$$F(k) = \int_{-\infty}^{\infty} f(x)e^{ikx} dx \quad (5)$$

is known as the **Fourier transform** of $f(x)$ and is often represented as $Tf(x)$. So we can write $F(k) = Tf(x)$ in shorthand. The same works for three dimensional functions as well, with \mathbf{r} and k , integrated over the corresponding volume, dV .

So long as the product of functions, $f(x)e^{ikx}$, neither tends to infinity nor diverges with x , the area under the integrand in (5) can easily be calculated. For different values of k then, e^{ikx} , and hence the area under the curve, keeps changing. This shows how an FT moves between variables x and k , geometrically.

The actual definition of an FT sees a constant factor of $(2\pi)^{-1}$ or $(2\pi)^{-1/2}$ on the right-hand side. In studies of XRD, however, this is usually ignored as it is nothing more than a scaling factor.

2.4 An example FT with the top hat function

Consider a function described as

$$f(x) = \begin{cases} 0 & \text{if } -\infty < x < -x_0 \\ h & \text{if } -x_0 < x < x_0 \\ 0 & \text{if } x_0 < x < \infty \end{cases}$$

which looks like a top hat (hence the name). Our intention here is to see what $Tf(x)$ would look like.

We redefine our limits in (5) as $-x_0$ to x_0 since $f(x)$ does not exist outside this.

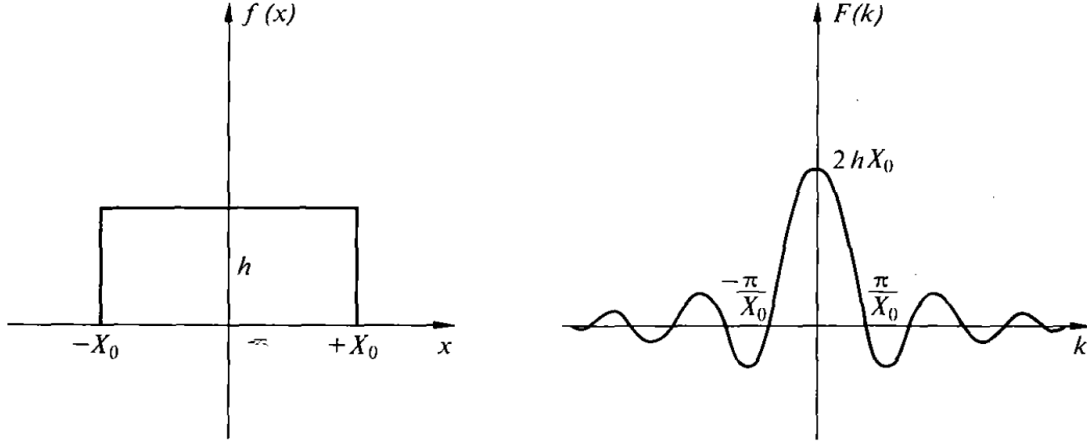


Figure 3: A top hat function, $f(x)$, and its $Tf(x)$. Figure borrowed from [B2].

As a result we only concern ourselves with the $f(x) = h$ part,

$$\begin{aligned}
 F(k) &= h \int_{-x_0}^{x_0} e^{ikx} dx \\
 &= h \left(\frac{e^{ikx}}{ik} \right) \Big|_{-x_0}^{x_0} \\
 &= h \left(\frac{e^{ikx_0} - e^{-ikx_0}}{ik} \right)
 \end{aligned}$$

Using $\sin x = (e^{ix} - e^{-ix})/2i$ we can write

$$F(k) = 2h \frac{\sin kx_0}{k} \quad \text{or} \quad F(k) = 2hx_0 \frac{\sin kx_0}{kx_0}$$

giving a function of the form $\sin x/x$ which is shown in fig. 3 along with $Tf(x)$. The height of the function, i.e. its amplitude, is given by $2hx_0$, and the width of the first peak is from the width between the first $x = 0$ points on either side of the origin. These occur when $\sin kx_0 = 0$ or $kx_0 = \pi$, giving us a width of $-\pi/x_0$ to π/x_0 , or simply $k = 2\pi/x_0$.

Fig. 3 shows our top hat function and its FT. Note how the width of $Tf(x)$ is less than that of $f(x)$. In fact, as $f(x)$ widens, $Tf(x)$ narrows and vice versa; this is characteristic of all FT. This is actually a general case: *the wider or more extended a function, the narrower is its Fourier transform; the narrower a function, the wider is its Fourier transform.*

This inverse, or reciprocal, relation in FT should bring to mind our discussions in §1, where we examined the reciprocal relationship between the real and reciprocal lattice vectors mathematically.

2.5 Inverse Fourier transforms

Interestingly, the function $F(k) = \mathcal{T}f(x)$ is also related as $f(x) = \mathcal{T}^{-1}F(k)$, i.e.,

$$f(x) = \int_{-\infty}^{\infty} F(k)e^{-ikx} dx \quad (6)$$

Numerically, however, (5) and (6) are not mutually related. In fact, for some $f(x)$, the transforms are related as

$$F(k) = \int_{-\infty}^{\infty} f(x)e^{ikx} dx \quad \text{and} \quad f(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} F(k)e^{-ikx} dx$$

or, just as effectively,

$$F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x)e^{ikx} dx \quad \text{and} \quad f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} F(k)e^{-ikx} dx$$

however, in XRD studies, the $1/\sqrt{2\pi}$ factor is usually left out since, as we discussed in §2.3 all it does is scale the equations.

2.6 Significance of Fourier transforms

We can be just as loose in handling the rest of the transform equation: the e^{ikx} factor can change signs too, just so long as we keep the opposite sign on the corresponding inverse transform.

All of this easy inter-convertibility between $f(x)$ and $F(k)$ tells us that they both contain the same information. As an exercise, one could easily work out the FT of the equation for $F(k)$ in our example in §2.4 and arrive back at $f(x)$.

For some \mathbf{r} in real space, the wave vector $\mathbf{k} = 2\pi/\lambda$ has a dimension of $[\text{L}]^{-1}$. The new coördinate system thus formed is simply the reciprocal analogue of the more familiar real space and is known either as the **k Space**, or the **reciprocal space** or the **Fourier space**. It is in this space that our reciprocal lattice lies.

Although helpful, an FT can give rise to certain problems that prevents us from extracting all possible information from it. This and other characteristics of an FT are best seen along the way, as they appear, rather than collected together in one section, alienated from their habitat.

3 Other useful mathematical analyses

Besides just Fourier transforms, it helps to first understand certain other mathematical tools and how they work with Fourier transforms before going ahead with our discussion on lattices.

3.1 Delta functions

A delta function, specifically a **Dirac delta function**, represented as $\delta(x - x_0)$ is any function that has a value of one at $x = x_0$ and zero everywhere else. The case where $x_0 = 0$ is particularly useful: if $x = 0$ the Dirac delta is one, else it is zero.

Right off the bat it is helpful to know why Delta functions are of interest to us. If a lattice represents an array of points in space, we can think of each point as a delta function. Therefore, a lattice point exists where a delta function exists. Identifying delta functions should therefore help us find the structure of our lattice.

We know that the real lattice vector

$$\mathbf{r} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c} \quad (1)$$

describes our unit cell (whether primitive or not) and, through it, our entire lattice. Written as a delta function,

$$L(\mathbf{r}) = \sum_{\mathbf{p}, \mathbf{q}, \mathbf{r}} \delta(\mathbf{r} - [u\mathbf{a} + v\mathbf{b} + w\mathbf{c}]) \quad (7)$$

The product of some $f(x)$ and $\delta(x - x_0)$ is $f(x_0)$ based on our discussion in §2.2, especially since the delta function does not exist anywhere else. As a result,

$$\int_{-\infty}^{\infty} f(x) \delta(x - x_0) dx = f(x_0) \quad (8)$$

and likewise for the three dimensional \mathbf{r} .

Suppose, in the above equation, that $f(x) = e^{ikx}$. We then have our FT equation, i.e. the FT of a single delta function:

$$F(k) = \int_{-\infty}^{\infty} e^{ikx} \delta(x) dx$$

which (8) simply requires that we calculate $f(0)$ since the delta function is $\delta(x - 0)$, i.e. $e^{ik0} = 1$, giving us

$$F(k) = 1$$

which means that a delta function at the origin has, as its FT, a constant one.

What about two delta functions, $\delta(x - x_0)$ and $\delta(x + x_0)$ then? That is, what

about $f(x) = \delta(x - x_0) + \delta(x + x_0)$? In the same manner as above,

$$\begin{aligned}
 F(k) &= \int_{-\infty}^{\infty} f(x) e^{ikx} dx \\
 &= \int_{-\infty}^{\infty} \delta(x - x_0) e^{ikx} dx + \int_{-\infty}^{\infty} \delta(x + x_0) e^{ikx} dx \\
 &= e^{-ikx_0} + e^{ikx_0}
 \end{aligned}$$

since $\cos x = \frac{e^{ix} + e^{-ix}}{2}$ we have $F(k) = 2 \cos kx_0$ (9)

In other words, the FT of two delta functions equidistant from the origin is a cosine function with peaks at ± 2 and a width of $\pi/2x_0$ to $-\pi/2x_0$.

The FT of three delta functions, i.e. $f(x) = \delta(x - x_0) + \delta(x) + \delta(x + x_0)$, can similarly be shown to be $F(k) = 1 + 2 \cos kx_0$. This argument can be extended to n delta functions as well as an infinite number of them.

Some points of note:

1. The spacing of the peaks in $F(k)$ is determined by the spacing of the delta functions
2. The width of the peaks in $F(k)$ is determined by the number of delta functions
3. The number of subsidiary peaks in $F(k)$ is determined by the number of delta functions

3.2 Symmetries in crystals

The knowledge of the presence of rotational etc. symmetries and mirror planes in lattices is a prerequisite for this discussion and will not be discussed here.

However, a selective look at some basic symmetries is warranted at this point:

Symmetric functions are functions of the form $f(-x) = f(x)$.

Antisymmetric functions are symmetric functions given by $f(-x) = -f(x)$.

Non-symmetric functions are not symmetric about any axis.

Centrosymmetric functions are those functions which are invertible about the origin and are symmetric in three dimensions with $f(-\mathbf{r}) = f(\mathbf{r})$

Consider the function $f(x) = \delta(x - x_0) - \delta(x + x_0)$, which is an antisymmetric function³. Our interest now is in seeing how the FT of symmetric (9) and antisymmetric functions might differ. For our new antisymmetric function we have,

$$\begin{aligned} F(k) &= \int_{-\infty}^{\infty} f(x)e^{ikx} dx \\ &= \int_{-\infty}^{\infty} \delta(x - x_0)e^{ikx} dx - \int_{-\infty}^{\infty} \delta(x + x_0)e^{ikx} dx \\ &= e^{-ikx_0} - e^{ikx_0} \end{aligned}$$

since $\sin x = \frac{e^{ix} - e^{-ix}}{2i}$ we have $F(k) = 2i \sin kx_0$ (10)

Comparing this to (9) we find a pattern that can, in fact, be generalised:

1. The FT of symmetric functions, as in (9), is real.
2. The FT of antisymmetric functions, as in (10), is imaginary.
3. The FT of non-symmetric functions, by extension (although this is verifiable), is complex, with a real and an imaginary part.

For the time being treat these as properties. As we go further we will realise how this can be used to identify various characteristics of a crystal and narrow our search down in steps to finally arrive the correct structure.

3.3 Convolutions

Another important class of functional operations we will be encountering are called **convolutions**. These are represented by $*$ and are not to be confused with the product of two functions. The convolution of $f(\mathbf{r})$ and $g(\mathbf{r})$ is defined as

$$f(\mathbf{r}) * g(\mathbf{r}) = \int_{\mathbf{r}} f(\mathbf{r})g(\mathbf{u} - \mathbf{r}) d\mathbf{r}$$

and it does not matter which variable takes the argument $(\mathbf{u} - \mathbf{r})$.

As before, we try to understand, geometrically, what is happening when we perform a convolution on two functions.

1. Given $f(\mathbf{r})$ and $g(\mathbf{r})$, invert $g(\mathbf{r})$ through the origin (or the y-axis in case of $g(x)$ and $f(x)$ in one dimension) to get $g(-\mathbf{r})$.

³Compare this with our example of two delta functions in §3.1 and note the change in sign.

2. Move $g(-\mathbf{r})$ through a distance of \mathbf{u} to get $g(\mathbf{u} - \mathbf{r})$
3. Multiply $f(\mathbf{r})$ and $g(\mathbf{u} - \mathbf{r})$ as in §2.2
4. Integrate over \mathbf{r} , i.e. find the area under the function obtained in the last step
5. Repeat the last three steps for various values of \mathbf{u}

Returning to our delta functions, the convolution two delta functions with some $g(x)$, i.e. $[\delta(x - x_0) + \delta(x + x_0)] * g(x)$, is

$$\begin{aligned} f(x) * g(x) &= \int_{-\infty}^{\infty} \delta(x - x_0)g(u - x) dx + \int_{-\infty}^{\infty} \delta(x + x_0)g(u - x) dx \\ &= g(u + x_0) + g(u - x_0) \end{aligned}$$

which is simply the function $g(x)$ centred at the delta functions, $\pm x_0$. Generally, the convolution of a function with any number of delta functions serves to centre that function around each of the delta functions.

Coming to crystals then, any **unit cell function**, $U(\mathbf{r})$, describes the unit cell of a lattice. And the lattice function (7), $L(\mathbf{r})$, describes the various points of a lattice as a series of delta functions. Putting two and two together, the convolution of the lattice function and the unit cell function will then place the unit cell structure at every point of the lattice as suggested by the lattice function, thereby building up our crystal structure. This is known as the **crystal structure function**, $C(\mathbf{r})$, and is given by

$$C(\mathbf{r}) = L(\mathbf{r}) * U(\mathbf{r}) \quad (11)$$

The FT of a convolution is described by the **convolution theorem** which is made up of two statements:

1. The convolution of two Fourier transforms is the Fourier transform of their product
2. The Fourier transform of a convolution is the product of their Fourier transforms

that is, mathematically,

$$[Tf(x)]*[Tg(x)] = T[f(x) \cdot g(x)] \quad \text{and} \quad T[f(x)*g(x)] = [Tf(x)] \cdot [Tg(x)] \quad (12)$$

4 X-ray scattering I

An X-ray interacts with an electron primarily in two ways: **Thomson scattering** and **Compton scattering**. The former is a purely classical effect (and is also called coherent scattering as we will soon see) while the latter is entirely a quantum mechanical effect (also called incoherent scattering).

4.1 Thomson scattering

The incident electromagnetic wave (X-ray) described by the vector \mathbf{E}_i causes an electron to experience oscillatory acceleration:

$$\mathbf{a} = \frac{e}{m} \mathbf{E}_i$$

This acceleration, like the acceleration of any charged particle, causes the electron to radiate. These waves are called **scattered waves** and are described by the vector \mathbf{E}_s which is related to \mathbf{E}_i as

$$\frac{\mathbf{E}_s}{\mathbf{E}_i} = \frac{e^2}{4\pi\epsilon_0 r m c^2} \frac{(1 + \cos^2 2\theta)}{2} \quad (13)$$

where \mathbf{r} is the distance between the electron which is the source of the field and the observer; 2θ is the angle of scatter of the X-rays, making θ the Bragg angle.

This relationship between \mathbf{E}_s and \mathbf{E}_i suggests that they have a well-defined phase relation (a $+$ would denote that the wave vectors are in-phase while a $-$ would denote that they are π out of phase).

4.2 Electronic scattering factor

Assuming Thomson scattering fully describes the scattering occurring due to an electron or a set of electrons (this is not always true and, when it is not, the effect is called anomalous scattering) we can define part of (13) as the **electronic scattering factor**,

$$f_e = \frac{e^2}{4\pi\epsilon_0 r m c^2} \quad (14)$$

In fact, so long as the incident X-ray is in a known state of polarisation, we can write (13) in terms of a **polarisation factor** that is a function only of θ as

$$\frac{\mathbf{E}_s}{\mathbf{E}_i} = f_e p(2\theta) \Rightarrow \frac{\mathbf{E}_s}{\mathbf{E}_i} \propto f_e$$

Assuming we only use unpolarised incident waves, though, $\mathbf{E}_s = f_e \mathbf{E}_i$ is sufficient to describe electronic scattering.

Suppose for the same incident X-ray there is a phase difference of some $e^{i\phi}$ between the waves scattered by two electrons, A and B, we can re-write our equation as $(\mathbf{E}_s)_A = f_e \mathbf{E}_i$ and $(\mathbf{E}_s)_B = f_e \mathbf{E}_i e^{i\phi}$ and their total scattering can simply be summed:

$$(\mathbf{E}_s)_{\text{Total}} = [f_e + f_e e^{i\phi}] \mathbf{E}_i$$

Extending this to a collection of n electrons, we have the relationship

$$\frac{\mathbf{E}_s}{\mathbf{E}_i} = \sum_n f_e e^{i\phi}$$

Interestingly, this is comparable to our FT equation written in three dimensions as

$$F(\Delta k) = \int_{-\infty}^{\infty} f(\mathbf{r}) e^{i\Delta \mathbf{k} \cdot \mathbf{r}} d\mathbf{r} \quad (5)$$

where ϕ is analogous to the phase factor $\Delta \mathbf{k} \cdot \mathbf{r}$ from our discussion of Bragg diffraction, and $f(\mathbf{r}) = f_e$ the amplitude function (see how we used this to describe the amplitude of the $F(k)$ versus x curve in §2.4) which specifies the ability of an obstacle (here, an electron) to scatter radiation.

In our sample, we may pick some elemental volume located at $d\mathbf{r}$ that contains an average number of electrons inside it as given by $\rho(\mathbf{r})$, called the **electron density function**. If the volume element is small enough we can safely assume that the wave incident on all the electrons and hence the scattered waves of all the electrons are in phase. The amplitude function, f_e , of one electron will then have to be re-written for all the electrons in the volume element as $f_e \rho(\mathbf{r})$, finally giving us

$$F(\Delta k) = \int_{-\infty}^{\infty} f_e \rho(\mathbf{r}) e^{i\Delta \mathbf{k} \cdot \mathbf{r}} d\mathbf{r} \quad (15)$$

4.3 Electron structure factor

The position of any unit cell point is given by

$$\mathbf{r} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c} \quad (1)$$

where $0 \leq u \leq 1$ and so on. This can be re-written in terms of some x , y and z with $x = u/a$ etc. so that we have $0 \leq x \leq 1$ and so on, giving us

$$\mathbf{r} = x\mathbf{a} + y\mathbf{b} + z\mathbf{c}$$

In other words, if u , v and w represent the **absolute position** of a point in a unit cell, x , y and z represent its **relative position**. The volume element, $d\mathbf{r}$, is then given by

$$d\mathbf{r} = dx dy dz \hat{\mathbf{a}} \cdot \hat{\mathbf{b}} \times \hat{\mathbf{c}} = V dx dy dz$$

letting us split our electron density function (15) across three dimensions as

$$F(\Delta \mathbf{k})_{rel} = F_{rel} = V \int_{x=0}^1 \int_{y=0}^1 \int_{z=0}^1 \rho(x, y, z) e^{i\Delta \mathbf{k} \cdot (x\mathbf{a} + y\mathbf{b} + z\mathbf{c})} dx dy dz \quad (16)$$

where the *rel* subscript reminds us that we are dealing with relative positions.

We saw in §1 that $\Delta \mathbf{k} = 2\pi \mathbf{G}_{hkl} = 2\pi (h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*)$ so the power of e in (16) becomes

$$\Delta \mathbf{k} \cdot (x\mathbf{a} + y\mathbf{b} + z\mathbf{c}) = 2\pi (h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*) \cdot (x\mathbf{a} + y\mathbf{b} + z\mathbf{c}) = 2\pi(hx + ky + lz)$$

so our equation corresponding to a reciprocal point described by h, k, l becomes

$$[F(\Delta\mathbf{k})_{rel}]_{hkl} = F_{hkl} = V \int_0^1 \int_0^1 \int_0^1 \rho(x, y, z) e^{2\pi i(hx+ky+lz)} dx dy dz \quad (17)$$

where F_{hkl} is known as the (geometrical) **structure factor** of the unit cell. As suggested by the power of e , it is a complex quantity with a magnitude of $|F_{hkl}|$ and a phase factor of $\alpha_{h,k,l}$ (say) that can be simply written as $F_{hkl} = |F_{hkl}| e^{i\alpha_{hkl}}$. The importance of the structure factor stems from the fact that it is related to the intensity (I_{hkl}) of its corresponding diffraction peak observed on an XRD pattern:

$$I_{hkl} = |F_{hkl}|^2 \quad (18)$$

closely linking an experimental outcome (the XRD pattern) with the theoretically described crystal structure (given in terms of h, k, l etc.). This is largely what lets us rebuild the structure of a crystal using a diffraction pattern obtained during an experiment.

4.4 Electron density function

Since the relationship between F_{rel} and $\rho(x, y, z)$ is an FT (16), we can write it as an inverse FT as well:

$$\begin{aligned} \rho(x, y, z) &= \frac{1}{V} \int_{\mathbf{k}} F(\Delta\mathbf{k})_{rel} e^{-i\Delta\mathbf{k} \cdot (x\mathbf{a}+y\mathbf{b}+z\mathbf{c})} d(\Delta\mathbf{k}) \\ &= \frac{1}{V} \int_{\mathbf{k}} F(\Delta\mathbf{k})_{rel} e^{-2\pi i(hx+ky+lz)} d(\Delta\mathbf{k}) \quad (\text{for the same reasons as in §4.3}) \end{aligned}$$

We can sum rather than integrate since the reciprocal lattice points are discrete and not continuous:

$$\rho(x, y, z) = \frac{1}{V} \sum_h \sum_k \sum_l F_{hkl} e^{-2\pi i(hx+ky+lz)} \quad (19)$$

4.5 Compton scattering

One of the ideas we have taken for granted up to this point is that the scattered and incident X-rays are of the same wavelength. This is the basis for Bragg's law as well as for Ewald's construction, and this is what Thomson scattering tells us too.

Rather than rays, however, Compton scattering treats the entire event as a collision between a photon and an electron. This ties in with experimental observations that, sometimes, a scattered X-ray is found in two wavelengths rather than one: although one of the diffracted rays matches in wavelength to the incident X-ray, there exists a second ray with a wavelength slightly longer than the incident ray.

This treatment of the phenomenon as a particle collision means the phase difference, i.e. the coherence between rays, plays no part in Compton scattering. It is for this reason that we also call this incoherent scattering. However, this absence of a phase difference means diffraction (primarily a wave phenomenon) cannot be accounted for with Compton scattering. Instead, this type of scattering gives rise to a background radiation that does not affect the XRD pattern in any way.

5 X-ray scattering II

Having discussed how electrons scatter X-rays we move on to how atoms do the same. For some atomic nucleus that is at \mathbf{r}_j from the origin, and for an electron at \mathbf{R}_j from that nucleus, let the position vector of the electron from the origin be \mathbf{r} . Therefore, $\mathbf{r} = \mathbf{r}_j + \mathbf{R}_j$ where the subscript j denotes the j^{th} atom. Why this roundabout way of using an atom and then its electron instead of an electron directly? Simply because it is easier to locate an atom than it is to locate an electron.

We can now write the electron density function, $\rho(\mathbf{r})$, from §4.2 as the j^{th} **atomic electron density function**, $\rho_j(\mathbf{R}_j)$ or $\rho_j(\mathbf{r} - \mathbf{r}_j)$. This is for one atom. For the entire unit cell we have

$$\rho(\mathbf{r}) = \sum_j \rho_j(\mathbf{r} - \mathbf{r}_j)$$

The structure factor (17) now becomes

$$F_{hkl} = \int_{\text{unit cell}} \sum_j \rho_j(\mathbf{r} - \mathbf{r}_j) e^{2\pi i \mathbf{G}_{hkl} \cdot \mathbf{r}} d\mathbf{r} \quad (\text{using } \Delta \mathbf{k} = 2\pi \mathbf{G}_{hkl})$$

Assuming all nuclei are at fixed positions (this is untrue, strictly speaking, but a fair approximation for now since, except at extremely high temperatures, any motion of nuclei in a solid is only oscillatory with incredibly small amplitudes) we can write $d\mathbf{r} = d\mathbf{R}_j$ and, of course, $\mathbf{r} - \mathbf{r}_j = \mathbf{R}_j$ and, in the power of e , we have $\mathbf{r} = \mathbf{r}_j + \mathbf{R}_j$.

$$\begin{aligned} F_{hkl} &= \int_{\text{unit cell}} \sum_j \rho_j(\mathbf{R}_j) e^{2\pi i \mathbf{G}_{hkl} \cdot (\mathbf{r}_j + \mathbf{R}_j)} d\mathbf{R}_j \\ &= \int_{\text{unit cell}} \sum_j \rho_j(\mathbf{R}_j) e^{2\pi i \mathbf{G}_{hkl} \cdot \mathbf{r}_j} e^{2\pi i \mathbf{G}_{hkl} \cdot \mathbf{R}_j} d\mathbf{R}_j \quad (\text{splitting the power of } e) \end{aligned}$$

We now make two modifications:

1. The order of summation and integration can be reversed.
2. Since we are summing in the end, the integration need no longer be over the entire unit cell; we therefore can just as well integrate only over the j^{th} atom.

$$F_{hkl} = \sum_j e^{2\pi i \mathbf{G}_{hkl} \cdot \mathbf{r}_j} \int_{\text{atom}} \rho_j(\mathbf{R}_j) e^{2\pi i \mathbf{G}_{hkl} \cdot \mathbf{R}_j} d\mathbf{R}_j$$

The integral on the right-hand side varies by atom. It is, in other words, characteristic of every atom. We call this the **atomic scattering factor** and represent it by f_j , i.e.,

$$f_j = \int_{\text{atom}} \rho_j(\mathbf{R}_j) e^{2\pi i \mathbf{G}_{hkl} \cdot \mathbf{R}_j} d\mathbf{R}_j \quad (20)$$

5.1 Atomic structure factor

From (20) we can re-write the structure factor (17) as

$$F_{hkl} = \sum_j f_j e^{2\pi i \mathbf{G}_{hkl} \cdot \mathbf{r}_j}$$

and $\mathbf{G}_{hkl} \cdot \mathbf{r}_j = (h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*) \cdot (x_j\mathbf{a} + y_j\mathbf{b} + z_j\mathbf{c}) = (hx_j + ky_j + lz_j)$ which means our **atomic structure factor** is now

$$F_{hkl} = \sum_j f_j e^{2\pi i (hx_j + ky_j + lz_j)} \quad (21)$$

Unlike the first form of the structure factor (17) this alternate form (21) has a few notable differences: it corresponds to the position of an atom in particular and not to an arbitrary point; it is discrete and not continuous; and it ties in directly with the atomic positions in a lattice, which makes it a much more useful expression for XRD experiments in general.

5.2 Atomic scattering factor

The electronic scattering factor (14) gives us the ability of an electron to scatter an incident X-ray. In the same vein, (20) gives us the ability of an atom to scatter an incident X-ray. There are three possible models for an atom that we will now consider in turn, in an increasing order of realism. We will apply (20) to each of them and see the results. It will turn out that our approximations are close enough to the most realistic picture and so much simpler that we will end up favouring the approximation itself.

For simplicity we will write (20) without subscripts as

$$f_j = \int_{\text{atom}} \rho_j(\mathbf{R}) e^{2\pi i \mathbf{G}_{hkl} \cdot \mathbf{R}} d\mathbf{R} \quad (20)$$

and examine the phenomenon as three cases as follows:

1. *The electrons are concentrated at the nucleus.*

Suppose the j^{th} atom has Z_j electrons, i.e. its atomic number is Z , then we can treat the electron density function, $\rho_j(\mathbf{R})$, as a delta function with a strength of X_j

$$\rho_j(\mathbf{R}) = Z_j \delta(\mathbf{R})$$

Therefore (20) becomes

$$f_j = \int_{\text{atom}} Z_j \delta(\mathbf{R}) e^{2\pi i \mathbf{G}_{hkl} \cdot \mathbf{R}} d\mathbf{R}$$

where Z_j is a constant and $\int \delta(\mathbf{R}) e^{i\mathbf{k}\cdot\mathbf{R}} d\mathbf{R} = 1$ as we discussed in §3.1. So,

$$f_j = Z_j \quad (22)$$

2. *The electron distribution is spherically symmetric.*

This time round we assume spherical symmetry as opposed to nuclear concentration. We therefore use polar coördinates,

$$d\mathbf{R} = R^2 \sin \theta dR d\theta d\phi$$

where θ is the angle between \mathbf{G}_{hkl} and \mathbf{R} giving us

$$\begin{aligned} f_j &= \int_{\text{atom}} \rho_j(R) e^{2\pi i G_{hkl} R \cos \theta} R^2 \sin \theta dR d\theta d\phi \\ &= \int_0^{2\pi} d\phi \int_0^\infty R^2 \rho_j(R) \left[\int_0^\pi e^{2\pi i G_{hkl} R \cos \theta} \sin \theta d\theta \right] dR \end{aligned}$$

which reduces to

$$f_j = 2\pi \int_0^\infty R^2 \rho_j(R) \left(\frac{e^{2\pi i G_{hkl} R} - e^{-2\pi i G_{hkl} R}}{2\pi i G_{hkl} R} \right) dR$$

which looks like $\sin \varphi = (e^{i\varphi} - e^{-i\varphi})/2i$, therefore,

$$f_j = 2\pi \int_0^\infty R^2 \rho_j(R) \left[\frac{\sin 2\pi G_{hkl} R}{\pi G_{hkl} R} \right] dR$$

Using the relationship $G_{hkl} = \frac{2}{\lambda} \sin \theta$ we get

$$f_j = 2\pi \int_0^\infty R^2 \rho_j(R) \left[\frac{\sin \left(\frac{4\pi}{\lambda} \sin \theta \right) R}{\left(\frac{2\pi}{\lambda} \sin \theta \right) R} \right] dR$$

Putting

$$s = \frac{4\pi \sin \theta}{\lambda}$$

we get

$$f_j = 4\pi \int_0^\infty R^2 \rho_j(R) \left(\frac{\sin sR}{sR} \right) dR$$

For small angles then,

$$f_j = 4\pi \int_0^\infty \rho_j(R) R^2 dR$$

where $\rho_j(R)$ is the number density of electrons per unit volume and $4\pi \int R^2 dR$ is the volume of the spherical atom. In other words, we have arrived back at

$$f_j = Z_j$$

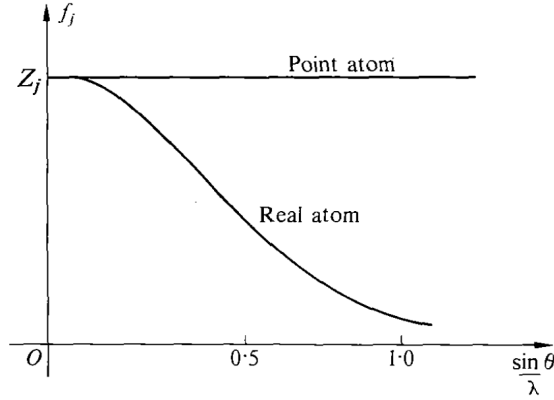


Figure 4: For model 1, $f_j = Z_j$ all the time. For other models, f_j falls off with an increase in Bragg angle.

The atomic scattering factor (f_j) is a function of $\frac{\sin \theta}{\lambda}$ and falls off if model 2 or 3 are applied, as shown ('real atom') in fig. 5.2. The exact values for f_j based on some θ can be determined using the *International tables for X-ray crystallography*.

3. *Non-spherically symmetric electron distribution.* The p, d and f orbitals are known to be non-spherically symmetric. However, for the most part the extra accuracy afforded by calculations of this measure are too small to justify. Generally, using $f_j = Z_j$ is good enough.

5.3 Anomalous scattering

As we saw in §3.2 (centro)symmetric functions have a real FT. However, in those conditions when Thomson scattering alone does not explain electronic scattering, i.e. when the energy of incident waves is just right and causes quantum effects in an atom by perturbing an electron, then the centrosymmetry is destroyed.

The non-symmetric function that now describes the electron distribution around an atom has a complex FT which can be represented as

$$f_j = (f_j)_C + \Delta f'' + i\Delta f''$$

where the term $(f_j)_C$ is the value of f_j calculated under the assumption of centrosymmetry; the term $\Delta f''$ is a real correction factor arising due to the perturbation of symmetry; and $i\Delta f''$ is, similarly, an imaginary correction factor. Both $\Delta f''$ and $i\Delta f''$ can be calculated theoretically.

5.4 Friedel's law

Consider the atomic structure factor equation:

$$F_{hkl} = \sum_j f_j e^{2\pi i (hx_j + ky_j + lz_j)} \quad (21)$$

For two atoms at (hkl) and $(\bar{h}\bar{k}\bar{l})$ we have the above equation and

$$F_{\bar{h}\bar{k}\bar{l}} = \sum_j f_j e^{-2\pi i (hx_j + ky_j + lz_j)}$$

respectively. Given that $f_j = Z_j$ is real, $F_{\bar{h}\bar{k}\bar{l}}$ is simply F_{hkl}^* , i.e. the complex conjugate of F_{hkl} . These are, symmetrically, *reflections about a mirror plane*. As a result,

$$|F_{hkl}| = |F_{\bar{h}\bar{k}\bar{l}}| \quad (23)$$

Equation (23) is called Friedel's law.

Verbally, Friedel's law states that *the magnitudes of the structure factors of centrosymmetrically related reciprocal lattice points are equal.*

The law has an interesting implication. We saw earlier that F_{hkl} is related to the intensity, I_{hkl} , as

$$I_{hkl} = |F_{hkl}|^2 \quad (18)$$

which also takes the centrosymmetric position, \overline{hkl} , into consideration:

$$I_{hkl} = |F_{hkl}|^2 = I_{\overline{hkl}} \quad (24)$$

In other words, *the intensities of the diffraction maxima corresponding to centrosymmetrically related reciprocal lattice points are equal.*

What if, instead of having the $F_{hkl} = f_j e^{ihx+ky+lz}$ form, we have a complex form, $F_{hkl} = f_j e^{ihx+ky+lz} + |f_A| e^{i\alpha}$? Then F_{hkl} and $F_{\overline{hkl}}$ are no longer equal and Friedel's law breaks down.

5.5 Systematic absences

5.5.1 BCC crystals

Consider a BCC crystal. We can describe this using the origin $(0, 0, 0)$ and a body centre with respect to that origin $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Its structure factor is then given by

$$F_{hkl} = Z e^{2\pi i(hx+ky+lz)} = Z e^{2\pi i(0)} + Z e^{\pi i(h+k+l)}$$

where Z is the atomic number according to the approximation in (22) which we said was acceptable.

The sum $h + k + l$ is known to be an integral and can end up being either even or odd, i.e. $2n$ or $2n + 1$ for integral n . Therefore,

$$F_{hkl} = Z(1 + e^{2n\pi i}) = Z(1 + 1) = 2Z \quad (\text{Expanding } e \text{ in terms of sin and cos})$$

for the even case and

$$F_{hkl} = Z(1 + e^{(2n+1)\pi i}) = Z[1 + (e^{2n\pi i})(e^{\pi i})] = 0 \quad (\text{Expanding } e \text{ once again})$$

for the odd case. Refer [2] for details on expanding e in the two cases.

Diffractions corresponding to such F_{hkl} with odd $h+k+l$ sums have zero intensity since $I_{hkl} = |F_{hkl}|^2 = 0^2$ and are called **systematic absences**. Therefore, if we have a diffraction pattern where the observed diffractions arise only as a result of $h + k + l$ being even, we know that the crystal is of BCC type.

5.5.2 FCC crystals

We repeat the same process as in §5.5.1 but using $(0, 0, 0)$, $(\frac{1}{2}, \frac{1}{2}, 0)$, $(\frac{1}{2}, 0, \frac{1}{2})$ and $(0, \frac{1}{2}, \frac{1}{2})$ to describe an FCC lattice.

We then end up with four terms,

$$F_{hkl} = f_j(1 + e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)})$$

and four cases: either h , k and l are all even or all odd, or one among them is even or odd. These cases turn out to be

$$F_{hkl} = 4f_j \quad F_{hkl} = 4f_j \quad F_{hkl} = 0 \quad F_{hkl} = 0$$

since either the three sums are all even (in the first two cases), or two of them are odd (in the second and third cases). The working is same as in §5.5.1. Refer [2] for details on expanding e in the two cases.

In case of FCC crystals, therefore, systematic absences in a diffraction pattern occur for those lattice points which can be described by an (hkl) Miller index such that h , k and l are either all even or all odd.

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Appendices

A Some useful results

1. For instance, at $x = 2\lambda$, $e^{ikx} = 1$ and $f(x)$ is some $f(2\lambda)$, which means $f(x)e^{ikx} = f(2\lambda)$. In fact, this pattern is true for $x = 0, \pm\lambda, \pm n\lambda/2$, i.e. wherever e^{ikx} has a maxima or minima. That is, the graph of the product $f(x)e^{ikx}$ is a graph of the points joining various $\pm f(x)$ in the manner discussed.
2. Expanding e for §5.5.1 and §5.5.2 is done as

$$e^{2n\pi i} = \cos(2n\pi) + i \sin(2n\pi) = 1$$

for even cases and

$$e^{\pi i} = \cos(\pi) + i \sin(\pi) = -1$$

for odd cases.

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