

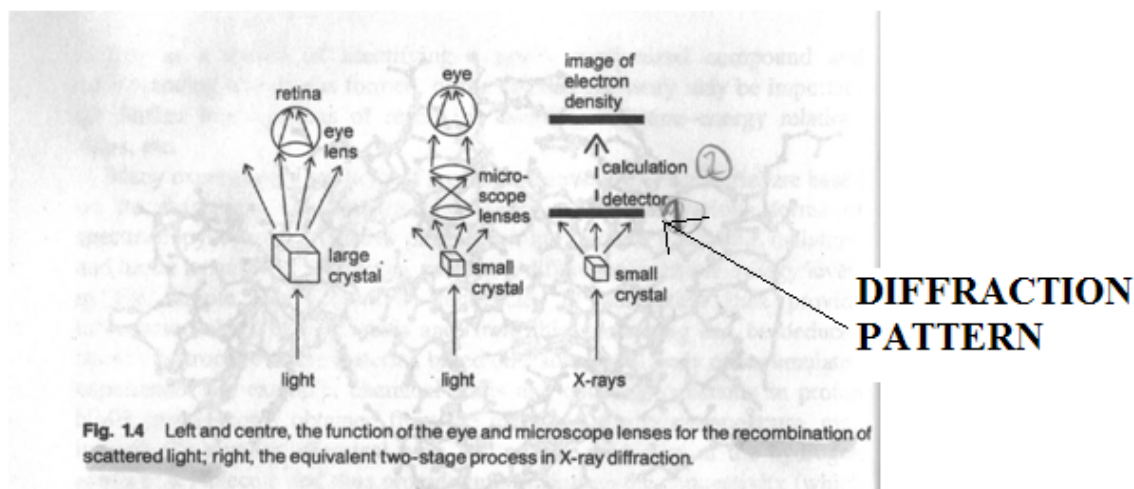
DETERMINATION OF CRYSTAL STRUCTURES BY X-RAY DIFFRACTION

1. GENERAL ASPECTS OF CRYSTAL STRUCTURE DETERMINATION

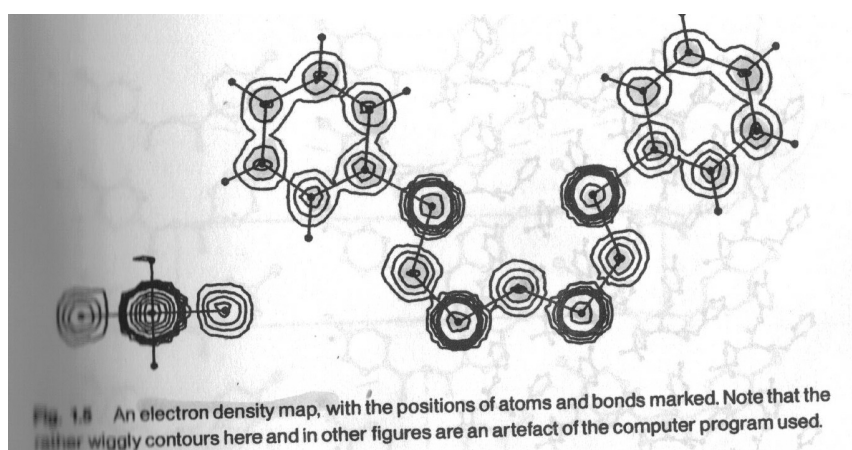
Many experimental methods for probing the structure of a material are based on its absorption and emission of radiation. These are various forms of spectroscopy. Absorption takes place when the frequency f of the radiation, and hence its quantum energy hf , matches a difference in certain energy levels in the sample. The observed frequencies of absorption therefore provide info about energy levels, and from this something can be deduced about the structure of the material. In most spectroscopic techniques, what is measured is the variation of intensity of radiation passing through the sample in a particular direction as its frequency is varied. The intensity variation is produced by absorption of particular frequencies, leading to energy changes in the sample.

In diffraction (light scattering) studies, we usually keep the wavelength fixed and measure the variation in intensity with direction, i.e. the scattering of monochromatic radiation is measured. From these measurements it is possible to get structural information about the sample like bond length, bond angles and torsion angles, and hence obtain a complete geometrical description of the crystal structure.

x-rays are the perfect candidates for resolving (viewing) atoms in crystal structures, which are of the order of one or a few angstroms in size (similar to the λ of X-rays). Using higher λ light would not in fact give enough scattering from atoms. The scattering of X-rays by molecules does occur but the scattered X-rays cannot be physically recombined to form an image because conventional lenses cannot be used to focus X-rays. The situation however is not hopeless because the pattern of scattered X-rays can be directly recorded, either on a photographic film or on a variety of other X-ray sensitive detectors, then the recombination which is impossible physically can be performed mathematically. Thus the experiment to determine a crystal structure falls into two parts: recording the X-ray diffraction pattern (single-crystal x-ray diffraction) and carrying out the recombination subsequently by mathematics, and is no longer instantaneous like viewing an object with a microscope.



This technique is collectively known as crystal structure determination. The object studied is typically a small crystalline sample (single crystal) rather than a single molecule, which would be impossible to hold in the X-ray beam for the duration of the experiment and which would give an immeasurably weak scattering pattern. In a crystal, there are a large number of identical molecules, locked in position in a periodic array, which together give significant scattering. The method can therefore only be used for samples which can be obtained in a suitably crystalline form. When the method is successful, it provides an image of the crystal structure. More precisely, it locates the components of the material which interact with the incident X-rays and scatter them. These are the electrons in the atoms. Although each individual electron/X-ray interaction is instantaneous, the total time taken to record the scattering pattern is usually hours or days, and this is very slow compared with the movement of electrons (due to thermal motion), so the picture that results is of a time-averaged electron density. Concentrations of electron density in the image correspond to atoms, somewhat spread out by time-averaged vibration.



One very important consequence of the need to divide the overall experiment into two parts instead of directly recombining the scattered X-rays to generate the real electron density image is that some of the information in the scattered x-rays is lost. When the x-ray diffraction pattern is recorded, the

individual scattered wave amplitudes are retained as relative intensities (intensity is proportional to the square of the amplitude), but the relative phases are lost. This makes the mathematical reconstruction stage much less straightforward. This is known as the phase problem, and there are methods to circumvent it.

The following points summarize the fundamental concepts of x-ray diffraction and properties of diffraction patterns:

- An object scatters radiation of λ comparable to its own size
- the mathematical relationship between the object and the scattering pattern is Fourier Transformation, such that the scattering pattern (in reciprocal space) is the Fourier Transform of the object (in real space), and the image of the object is in turn the Fourier Transform of the scattering pattern.
- If identical objects (basis) are arranged on a lattice, diffraction effects of the lattice are also imposed, so that the diffraction pattern can have non-zero intensity only where the direction of scattering satisfies the equations for diffraction geometry. The overall effect is the combination of the two effects—scattering by the object further restricted by diffraction by the lattice, so the observed diffraction pattern is the Fourier transform of the single object sampled at certain geometrically determined points.

In principle then the process of crystal structure determination is simple. We record the diffraction pattern from a crystal. Measurement of the diffraction pattern geometry and symmetry tells us the unit cell geometry and gives us some information about the symmetry of arrangement of the molecules in the unit cell. Then from the individual intensities of the diffraction pattern we work out the positions of the atoms in the unit cell, adding together the individual waves with their correct relative amplitudes and phases. And here we see the phase problem, the fact that the measured diffraction pattern provides directly only the amplitudes and not the required phases, without which the Fourier Transformation cannot be made to find real image of the crystal structure.

2. RECIPROCAL LATTICE

The **lattice reciprocal to a Bravais lattice (reciprocal lattice)** plays a fundamental role in most analytic studies of periodic structures. It has applications in many fields of crystal analysis, but in this context we will apply it to the theory of the **diffraction of X rays by a crystal** **X-ray diffraction methods for crystal structure determination**

Consider a set of Bravais lattice vectors \mathbf{R} constituting a Bravais lattice, and a plane wave $e^{i\mathbf{k}\cdot\mathbf{r}}$. For a general \mathbf{k} such a plane wave will not, of course, have the periodicity of the Bravais lattice, but for certain special choices of \mathbf{k} it will.

DEFINITION OF RECIPROCAL LATTICE OF A BRAVAIS LATTICE: The set of all wave vectors K (or G) that yield plane waves with the periodicity of a given Bravais lattice. K are known as the **Reciprocal lattice vectors**. Analytically K belongs to the reciprocal lattice of a Bravais lattice of points R , provided that the relation

$$e^{i\mathbf{K} \cdot (\mathbf{r} + \mathbf{R})} = e^{i\mathbf{K} \cdot \mathbf{r}}$$

holds for any \mathbf{r} , and for all \mathbf{R} in the Bravais lattice. Factoring out $e^{i\mathbf{K} \cdot \mathbf{r}}$, we can characterize the reciprocal lattice as the set of wave vectors K satisfying:

$$e^{i\mathbf{K} \cdot \mathbf{R}} = 1$$

for all \mathbf{R} in the Bravais lattice.

Note that a reciprocal lattice is defined with reference to a particular Bravais lattice. The Bravais lattice that determines a given reciprocal lattice is often referred to as the **direct lattice**, when viewed in relation to its reciprocal.

Vectors in the direct lattice have the dimensions of [length]; vectors in the reciprocal lattice have the dimensions of [1/length]. The reciprocal lattice is a lattice in the **Fourier (reciprocal) space** associated with the crystal. Wavevectors are always drawn in Fourier space, so that every position in Fourier space may have a meaning as a description of a wave. \mathbf{r} and \mathbf{k} are therefore referred to as a pair of reciprocal (conjugated) coordinates.

FOURIER FORMALISM FOR RECIPROCAL LATTICES

The above definition of the reciprocal lattice connects naturally to the definition of Fourier series of a periodic function. A Bravais lattice is **invariant** under the following type of translational symmetry transformations: $\mathbf{T} = u_1\mathbf{a}_1 + u_2\mathbf{a}_2 + u_3\mathbf{a}_3$, where the u s are integers and the \mathbf{a} s are the primitive translation vectors of the Bravais lattice. \mathbf{T} corresponds to the displacement vectors between any two Bravais lattice points (i.e. sum or difference of any two Bravais lattice vectors, including the Bravais lattice vectors \mathbf{R} themselves). \mathbf{T} therefore represents the **periodicity** of the Bravais lattice. As a result, any local physical property of the crystal is invariant (periodic) under \mathbf{T} , such as the charge concentration, electron number density, or magnetic moment density. Let n be any function expressing any local physical property of the Bravais lattice (e.g. electron number density):

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

n =PERIODIC FUNCTION WITH PERIOD \mathbf{T}

Being a periodic function, n can be expressed as a Fourier Series.

Take first a 1D function $n(x)$ with period a in the direction x . Expressing $n(x)$ as a Fourier Series :

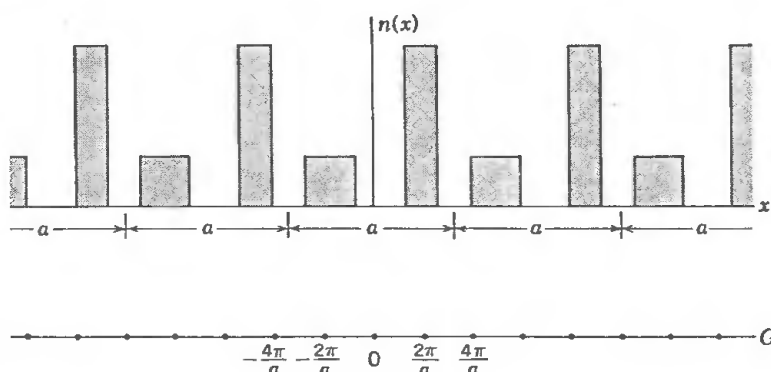
$$n(x) = n_0 + \sum_{p>0} [C_p \cos(2\pi p x/a) + S_p \sin(2\pi p x/a)]$$

where the p s are the positive integers denoting the various basis functions of the sine-cosine OBS and C_p, S_p are real constants, called the Fourier coefficients of the expansion. The factor $2\pi/a$ in the arguments ensures that $n(x)$ has the period a :

$$\begin{aligned} n(x+a) &= n_0 + \sum [C_p \cos(2\pi p x/a + 2\pi p) + S_p \sin(2\pi p x/a + 2\pi p)] \\ &= n_0 + \sum [C_p \cos(2\pi p x/a) + S_p \sin(2\pi p x/a)] = n(x) . \end{aligned}$$

We say that $2\pi p/a$ is a point in the reciprocal lattice or Fourier space of the Bravais lattice. In one dimension these points lie on a line. The reciprocal lattice points tell us the allowed terms in the Fourier series (the terms consistent with the periodicity of the crystal). Other points in the reciprocal space are not allowed in the Fourier expansion of a periodic function.

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 magnitudes of the individual terms n_p are not plotted.



It is a great convenience to write the series D) in the compact form:

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

where the sum is over all integers p : positive, negative and zero. The coefficients n_p are now complex numbers. To ensure that $n(x)$ is a real function, we require:

$$n_{-p}^* = n_p .$$

for then the sum of the terms in p and $-p$ is real. The asterisk on n_p^* denotes the complex conjugate of n_p . The Fourier coefficients are given by:

$$n_p = a^{-1} \int_0^a dx \, n(x) \exp(-i2\pi p x/a) .$$

The extension of the Fourier analysis to periodic functions $n(\mathbf{r})$ in 3D with period T is straightforward.:

Any periodic function $n(\mathbf{r})$ with the periodicity T of the Bravais lattice can be expressed as the following Fourier Series:

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

where \mathbf{G} are all the possible reciprocal lattice vectors

The Fourier coefficients are given by:

$$n_{\mathbf{G}} = V_c^{-1} \int_{\text{cell}} dV \, n(\mathbf{r}) \exp(-i\mathbf{G} \cdot \mathbf{r}) .$$

Here V_c is the volume of a unit cell of the Bravais lattice.

Using this 3D form of the Fourier Series it's easy to see the connection with the definition of reciprocal lattice as the set of all wave vectors \mathbf{K} that yield plane waves with the periodicity T of a given Bravais lattice, as these plane waves are the only terms which can appear in $n(\mathbf{r}) = \sum_{\mathbf{G}} n_{\mathbf{G}} \exp(i\mathbf{G} \cdot \mathbf{r})$ for the Fourier series representation of the electron density to have the desired invariance under any crystal translation \mathbf{T} . (plane waves are Fourier components of $n(\mathbf{r})$ and therefore must have the same periodicity T of n)

Proof:

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

$$\exp(i\mathbf{G} \cdot \mathbf{T}) = 1,$$

But (from the condition that the plane wave $e^{i\mathbf{G}\cdot\mathbf{r}}$ has periodicity T). Hence $n(\mathbf{r} + \mathbf{T}) = n(\mathbf{r})$ as required. This result proves that the Fourier representation of a function periodic in the Bravais lattice can contain components $n_{\mathbf{G}} \exp(i\mathbf{G} \cdot \mathbf{r})$ only at the reciprocal lattice vectors \mathbf{G}

The reciprocal lattice is itself a Bravais lattice, according to both definitions of Bravais lattice. We can give a detailed proof of this, which also provides an explicit algorithm for constructing the reciprocal lattice. Let $\mathbf{a}_1, \mathbf{a}_2$, and \mathbf{a}_3 be a set of primitive translation vectors for the direct lattice. Then the reciprocal lattice can be generated by the following three reciprocal primitive translation vectors:

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

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

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

(NOTE THIS WORKS ONLY IF THE \mathbf{a} s AND \mathbf{b} s ARE PRIMITIVE

VECTORS OF THEIR RESPECTIVE LATTICES)

To verify that the above gives a set of primitive vectors for the reciprocal lattice, one first notes that the \mathbf{b}_i satisfy:

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij}, \quad \begin{aligned} \delta_{ij} &= 0, & i &\neq j; \\ \delta_{ij} &= 1, & i &= j. \end{aligned}$$

Now any vector \mathbf{k} can be written as a linear combination of the \mathbf{b}_i (which form a complete basis in reciprocal space):

$$\mathbf{k} = k_1\mathbf{b}_1 + k_2\mathbf{b}_2 + k_3\mathbf{b}_3.$$

If \mathbf{R} is a Bravais lattice vector then:

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3, \quad \text{where the } n\text{s are integers}$$

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij}, \longrightarrow \mathbf{k} \cdot \mathbf{R} = 2\pi(k_1n_1 + k_2n_2 + k_3n_3).$$

For $e^{i\mathbf{k} \cdot \mathbf{R}}$ to be unity for all \mathbf{R} as required for a reciprocal lattice, $\mathbf{k} \cdot \mathbf{R}$ must be 2π times an integer for any choices of the integers n . This requires the coefficients k_i to be integers. Thus the condition

$e^{i\mathbf{k} \cdot \mathbf{R}} = 1$ that \mathbf{K} be a reciprocal lattice vector is satisfied by just those vectors for which:

RECIPROCAL LATTICE VECTORS: $\underline{\mathbf{K}} = k_1\underline{\mathbf{b}}_1 + k_2\underline{\mathbf{b}}_2 + k_3\underline{\mathbf{b}}_3$ where the k s are integers

Thus the reciprocal lattice is a Bravais lattice and the \mathbf{b}_i can be taken as the reciprocal primitive translation vectors.

Since the reciprocal lattice is itself a Bravais lattice, one can construct its reciprocal !! (reciprocal of a reciprocal lattice). This turns out to be nothing but the original direct lattice. One way to prove this is by constructing the set of reciprocal primitive vectors \mathbf{c}_i out of the \mathbf{b}_i according to the same formulae for \mathbf{b}_i out of \mathbf{a}_i . It then follows from simple vector identities that $\mathbf{c}_i = \mathbf{a}_i$, $i=1,2,3$. A simpler proof follows from the basic definition of a reciprocal lattice, according to which The reciprocal of the reciprocal is the set of all vectors \mathbf{G} satisfying:

$$e^{i\mathbf{G} \cdot \mathbf{K}} = 1$$

for all \mathbf{K} in the reciprocal lattice. Since any direct lattice vector \mathbf{R} has this property, all direct lattice vectors are in the lattice reciprocal to the reciprocal lattice. Furthermore, no other vectors can be, for a vector not in the direct lattice has the form $\mathbf{r} = x_1\mathbf{a}_1 + x_2\mathbf{a}_2 + x_3\mathbf{a}_3$ with at least one non-integral x_i . For that value of i , $e^{i\mathbf{b}_i \cdot \mathbf{r}} = e^{2\pi i x_i} \neq 1$, and the condition is violated for the reciprocal lattice vector $\mathbf{K} = \mathbf{b}_i$.

IMPORTANT EXAMPLES

The simple cubic Bravais lattice, with cubic PUC of side a , has as its reciprocal a simple cubic lattice with cubic PUC of side $2\pi/a$.

Proof: consider the direct primitive translation vectors that form the sides of the PUC of the direct

Bravais lattice (Here $\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}$ are orthogonal vectors of unit length parallel to the cube edges):

$$\mathbf{a}_1 = a\hat{\mathbf{x}}, \quad \mathbf{a}_2 = a\hat{\mathbf{y}}, \quad \mathbf{a}_3 = a\hat{\mathbf{z}},$$

then $\mathbf{b}_1 = \frac{2\pi}{a} \hat{x}$, $\mathbf{b}_2 = \frac{2\pi}{a} \hat{y}$, $\mathbf{b}_3 = \frac{2\pi}{a} \hat{z}$.

The **face-centered cubic Bravais lattice** with a cubic CUC of side a has as its reciprocal a bcc lattice with cubic CUC of side $4\pi/a$.

Proof: consider the fcc primitive vectors $\mathbf{a}_1 = \frac{a}{2}(\hat{y} + \hat{z})$, $\mathbf{a}_2 = \frac{a}{2}(\hat{z} + \hat{x})$, $\mathbf{a}_3 = \frac{a}{2}(\hat{x} + \hat{y})$.

from which we get: $\mathbf{b}_1 = \frac{4\pi}{a} \frac{1}{2}(\hat{y} + \hat{z} - \hat{x})$, $\mathbf{b}_2 = \frac{4\pi}{a} \frac{1}{2}(\hat{z} + \hat{x} - \hat{y})$, $\mathbf{b}_3 = \frac{4\pi}{a} \frac{1}{2}(\hat{x} + \hat{y} - \hat{z})$

This has precisely the form of the bcc primitive vectors, provided the side of the cubic CUC is taken to be $4\pi/a$.

The **body-centered cubic lattice** with cubic CUC of side a has as its reciprocal lattice a fcc lattice with cubic CUC of side $4\pi/a$. This can be proved by direct construction of the reciprocal primitive vectors, but it also follows from the above result for the reciprocal of the fcc lattice, along with the theorem that the reciprocal of the reciprocal is the original lattice.

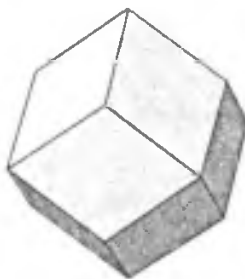
VOLUME OF THE RECIPROCAL PUC: If v is the volume of a PUC in the direct lattice, then the PUC of the reciprocal lattice has a volume $(2\pi)^3/v$.

FIRST BRILLOUIN ZONE OF A BRAVAIS LATTICE= The Wigner-Seitz PUC of the corresponding reciprocal lattice about the origin of the reciprocal space (for 1st zone), which is also the origin of real space

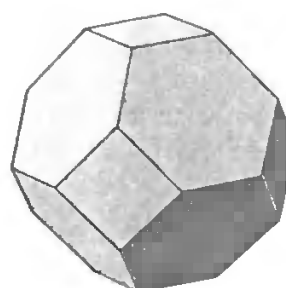
Thus, because the reciprocal of the bcc lattice is fcc, the 1st BZ of the bcc lattice is just the fcc WSUC. Conversely, the 1st BZ of the fcc lattice is just the bcc WSUC

Figure 5.2

- (a) The first Brillouin zone for the body-centered cubic lattice.
(b) The first Brillouin zone for the face-centered cubic lattice.



(a)



(b)

LATTICE PLANES

There is an intimate relation between vectors in the reciprocal lattice and planes of points in the direct lattice. This relation is important to understand the fundamental role that the reciprocal lattice plays in the theory of diffraction, and will be applied to that problem in the next section. Here we shall describe the relation in general geometrical terms.

Given a particular Bravais lattice, a **lattice plane** is defined to be any plane containing at least three noncollinear Bravais lattice points. Because of the translational symmetry of the Bravais lattice, any such plane will actually contain infinitely many lattice points, which form a 2D Bravais lattice within the plane. Some lattice planes in a simple cubic Bravais lattice are pictured below:

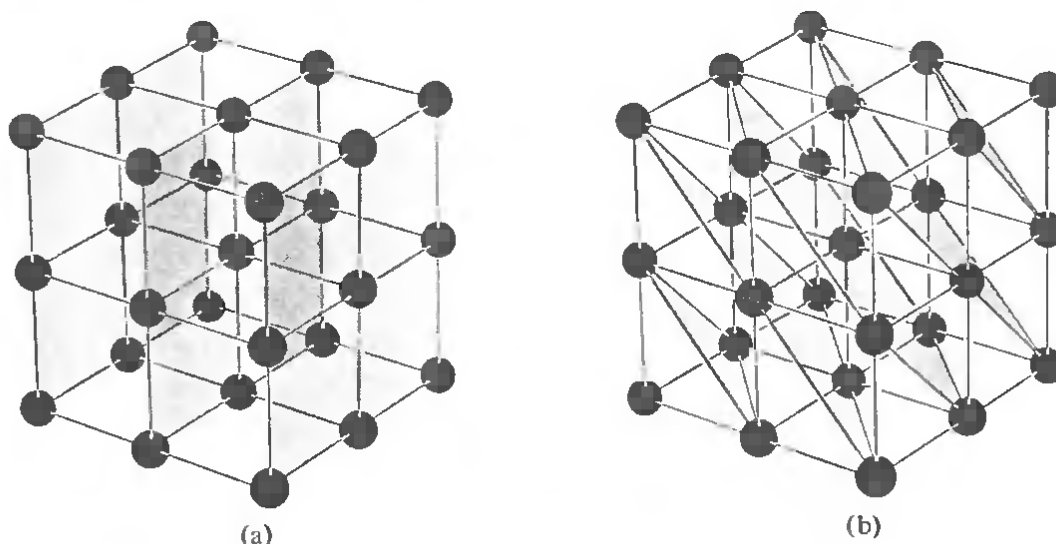


Figure 5.3

Some lattice planes (shaded) in a simple cubic Bravais lattice: (a) and (b) show two different ways of representing the lattice as a family of lattice planes.

By a **family of lattice planes** we mean a set of parallel, equally spaced lattice planes, which together contain all the points of the 3D Bravais lattice. Any lattice plane is a member of such a family. As can be seen from the pic above, there are many families of lattice planes for a given Bravais lattice. The reciprocal lattice provides a very simple way to classify all possible families of lattice planes, which is embodied in the following theorem:

For any family of lattice planes separated by a distance d , there are reciprocal lattice vectors perpendicular to the planes, the shortest of which have a length of $2\pi/d$. Conversely, for any reciprocal lattice vector K , there is a family of lattice planes normal to K and separated by a distance d , where $2\pi/d$ is the length of the shortest reciprocal lattice vector parallel to K

The theorem is a straightforward consequence of:

- the definition of reciprocal lattice vectors as the wave vectors of plane waves that are unity at all Bravais lattice sites $e^{i\mathbf{K} \cdot \mathbf{R}} = 1$
- The fact that a plane wave has the same value at all points lying in a family of planes that are perpendicular to its wave vector and separated by an integral number of wavelengths.

To prove the first part of the theorem, given a family of lattice planes, let $\hat{\mathbf{n}}$ be a unit vector normal to the planes. That $\mathbf{K} = 2\pi\hat{\mathbf{n}}/d$ is a reciprocal lattice vector follows from the fact that the plane wave $e^{i\mathbf{K} \cdot \mathbf{r}}$ is constant in planes perpendicular to \mathbf{K} and has the same value in planes separated by $\lambda = 2\pi/K = d$. Since one of the lattice planes contains the Bravais lattice point $\mathbf{r}=0$, $e^{i\mathbf{K} \cdot \mathbf{r}}$ must be unity for any point \mathbf{r} in any of the planes. Since the planes contain ALL Bravais lattice points, $e^{i\mathbf{K} \cdot \mathbf{R}} = 1$ for all \mathbf{R} , so that \mathbf{K} is indeed a reciprocal lattice vector. Furthermore, \mathbf{K} is the shortest reciprocal lattice vector normal to the planes, for any wave vector shorter than \mathbf{K} will give a plane wave with wavelength greater than $2\pi/K = d$. Such a plane wave cannot have the same value on all planes in the family, and therefore cannot give a plane wave that is unity at all Bravais lattice points.

To prove the converse of the theorem, given a reciprocal lattice vector, let \mathbf{K} be the shortest parallel reciprocal lattice vector. Consider the set of real space planes on which the plane wave $e^{i\mathbf{K} \cdot \mathbf{r}} = 1$. These planes (one of which contains the point $\mathbf{r}=0$) are perpendicular to \mathbf{K} and separated by a distance $d = 2\pi/K$. Since the Bravais lattice vectors \mathbf{R} all satisfy $e^{i\mathbf{K} \cdot \mathbf{R}} = 1$ for any reciprocal lattice vector \mathbf{K} , they must all lie within these planes. Furthermore the spacing between the lattice planes is also d (rather than some integral multiple of d), for if only every n th plane in the family contained Bravais lattice points, then according to the first part of the theorem, the vector normal to the planes of length $2\pi/nd$, i.e. the vector \mathbf{K}/n , would be a reciprocal lattice vector. This would contradict our original assumption that no reciprocal lattice vector parallel to \mathbf{K} is shorter than \mathbf{K} .

The correspondence between reciprocal lattice vectors and families of lattice planes is connected to the Miller index notation for the lattice plane. Quite generally one describes the orientation of a plane by giving a vector normal to the plane. Since we know there are reciprocal lattice vectors normal to any family of lattice planes, it is natural to pick a reciprocal lattice vector to represent the normal. To make the choice unique, one uses the shortest such reciprocal lattice vector. **It turns out that the Miller indices of a family of lattice planes are the coordinates of the shortest reciprocal lattice vector normal to that plane, with respect to a set of reciprocal primitive translation vectors.** Thus a plane with Miller indices h,k,l is normal to the reciprocal lattice vector $h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$. Note that this definition is consistent with the fact that Miller indices are integers, since any reciprocal lattice vector is a linear combination of three primitive vectors with integral coefficients. Note also that the Miller indices depend on the particular choice of primitive vectors.

To recombine this interpretation of miller indices in reciprocal space with the previous definition in real space, note that because a lattice plane with Miller indices h,k,l is normal to the reciprocal lattice vector $h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$, it will be contained in the continuous plane $\mathbf{K} \cdot \mathbf{r} = A$, for suitable choice of the constant A . This plane intersects the crystal axes determined by the direct lattice primitive vectors \mathbf{a}_i at the points $x_1\mathbf{a}_1$, $x_2\mathbf{a}_2$, and $x_3\mathbf{a}_3$, where the x_i are determined by the condition that $x_i\mathbf{a}_i$ indeed satisfy the equation of the plane: $\mathbf{K} \cdot (x_i\mathbf{a}_i) = A$. Since $\mathbf{K} \cdot \mathbf{a}_1 = 2\pi h$, $\mathbf{K} \cdot \mathbf{a}_2 = 2\pi k$, and $\mathbf{K} \cdot \mathbf{a}_3 = 2\pi l$, it follows that:

$$x_1 = \frac{A}{2\pi h}, \quad x_2 = \frac{A}{2\pi k}, \quad x_3 = \frac{A}{2\pi l}.$$

Thus the intercepts with the crystal axes of a lattice plane are inversely proportional to the Miller indices of the plane:

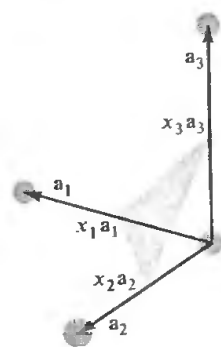


Figure 5.4

An illustration of the crystallographic definition of the Miller indices of a lattice plane. The shaded plane can be a portion of the continuous plane in which the points of the lattice plane lie, or any plane parallel to the lattice plane. The Miller indices are inversely proportional to the x_i .

proportional to the intercepts of the crystal plane along the crystal axes:

$$h:k:l = \frac{1}{x_1} : \frac{1}{x_2} : \frac{1}{x_3}.$$

3. MATHEMATICAL LAWS GOVERNING X-RAY DIFFRACTION: BRAGG AND VON LAUE LAWS

We study crystal structure through the diffraction of photons, neutrons, and electrons:

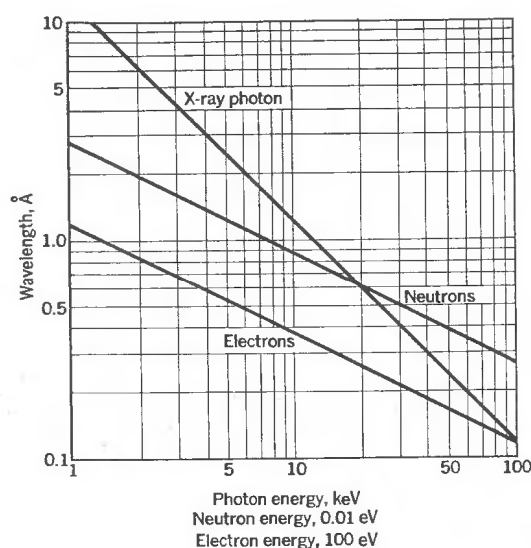


Figure 1 Wavelength versus particle energy, for photons, neutrons, and electrons.

The diffraction depends on the crystal structure and on the wavelength. At optical wavelengths such as 5000 Å the superposition of the waves scattered elastically by the individual atoms of a crystal results in ordinary optical refraction. When the wavelength of the radiation is comparable with or smaller than the lattice constant, we may find diffracted beams in directions quite different from the incident direction.

Typical interatomic distances in a crystal structure (distance between neighboring bases) are of the order of an angstrom (10^{-10} m). An EM probe of the microscopic structure of a solid must therefore have a wavelength at least this short, corresponding to an energy of the order:

$$\hbar\omega = \frac{hc}{\lambda} = \frac{hc}{10^{-8} \text{ cm}} \approx 12.3 \times 10^3 \text{ eV}.$$

Energies like this, on the order of several thousands of eV (keV) are characteristic X-ray energies

Another important difference between X-rays, electrons and neutrons part from their wavelength is their mechanism of interaction with the crystal structure:

- X-rays: interact with atomic electrons
- Neutrons: interact with the atomic nucleus
- Electrons: interact via Coulomb potential

We shall now see how the distribution of X-rays scattered by a rigid, periodic array of ions (crystal structure) reveals the locations of the ions within the structure. There are two equivalent ways to view the scattering of X-rays by a perfect periodic structure, due to Bragg and to von Laue, both of which are widely used. Both are described below, together with a proof of their equivalence

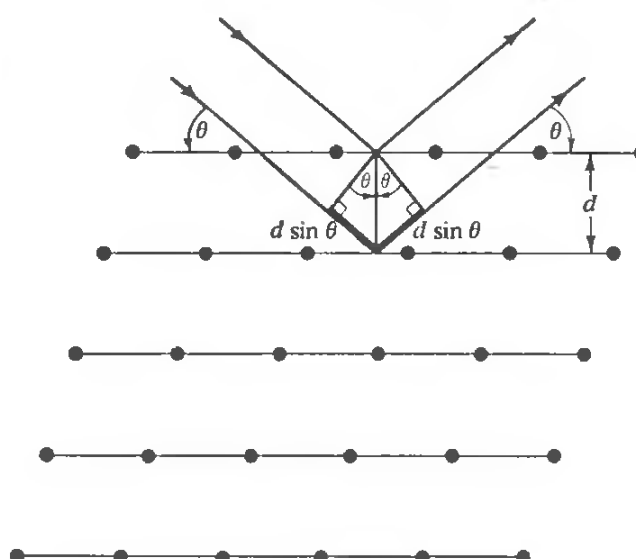
BRAGG FORMULATION OF X-RAY DIFFRACTION BY A CRYSTAL

Bragg found that substances whose macroscopic forms were crystalline gave remarkably characteristic patterns of diffracted X-radiation, quite unlike those produced by liquids (amorphous materials). In crystalline materials, for certain sharply defined wavelengths and incident directions, intense peaks of scattered radiation (Bragg peaks) were observed. This can be explained by treating the crystal structure as made out of parallel planes of ions (family of lattice planes passing through lattice points), spaced a distance d apart. The conditions for a sharp peak in the intensity of the scattered radiation are:

- The X-rays should be specularly reflected by the ions in any one plane (i.e. angle of incidence=angle of reflection, and the incoming and outgoing beams and the normal to the reflecting planes must themselves all lie in one plane).
- The reflected rays from successive planes should interfere constructively.

Figure 6.1

A Bragg reflection from a particular family of lattice planes, separated by a distance d . Incident and reflected rays are shown for the two neighboring planes. The path difference is $2d \sin \theta$.



For rays specularly reflected from adjoining planes, the path difference between the two rays is just $2d \sin \theta$, where θ is the angle of incidence.

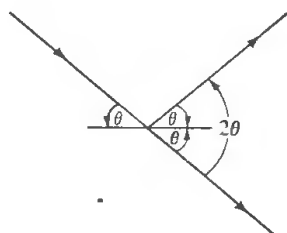


Figure 6.2

The Bragg angle θ is just half the total angle by which the incident beam is deflected.

For the rays to interfere constructively, this path difference must be an integral number n of wavelengths \diamond

BRAGG'S LAW

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

θ =Bragg angle=angle of incidence=angle of diffraction

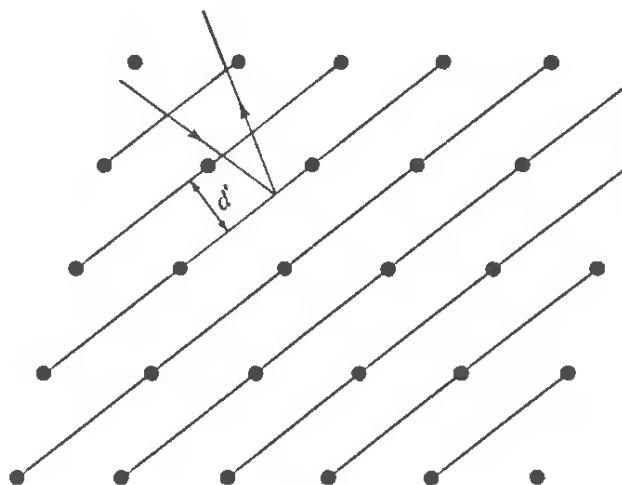
The angle of diffraction therefore depends on d and therefore on the structure of the sample

Bragg reflection can occur only for wavelengths $< 2d$. This is why we cannot use visible light. Although the reflection from each plane is specular, for only certain values of θ will the reflections from all parallel planes add up in phase to give a strong reflected beam. Each plane reflects only a very small fraction of the incident radiation. If each plane were perfectly reflecting, only the first plane of a parallel set would see the radiation, and any wavelength would be reflected. But each plane reflects 10^{-3} to 10^{-5} of the incident radiation, so that 10^3 to 10^5 planes may contribute to the formation of the Bragg-reflected beam in a perfect crystal.

The integer n is known as the order of the corresponding reflection. For a given set of parallel planes (which fixes d), one can see different orders of diffraction peaks by either varying λ or θ (or both). New diffraction peaks are obtained every time Bragg's Law is satisfied. Not only can one have higher-order reflections from a given set of lattice planes, but in addition one must recognize that there are many different ways of sectioning the crystal into planes (families of parallel planes with different values of d), each of which will itself produce further reflections. Remember that each family of lattice planes is labeled by a set of Miller Indices

Figure 6.3

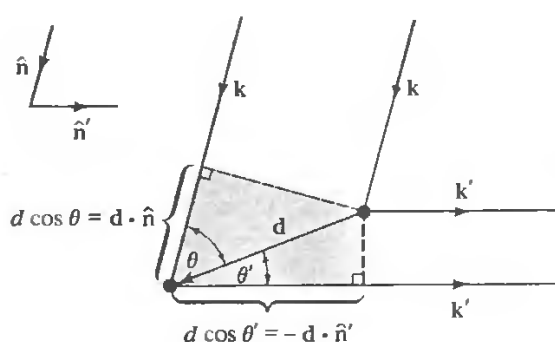
The same portion of Bravais lattice shown in Figure 6.1, with a different resolution into lattice planes indicated. The incident ray is the same as in Figure 6.1, but both the direction (shown in the figure) and wavelength (determined by the Bragg condition (6.2) with d replaced by d') of the reflected ray are different from the reflected ray in Figure 6.1. Reflections are possible, in general, for any of the infinitely many ways of resolving the lattice into planes.



VON LAUE FORMULATION OF X-RAY DIFFRACTION BY A CRYSTAL

The von Laue approach differs from the Bragg approach in that no particular sectioning of the crystal into lattice planes is singled out, and no ad hoc assumption of specular reflection is imposed. Instead one regards the crystal structure as composed of identical microscopic objects (set of ions or atoms) placed at the sites R of a Bravais lattice, each of which can reradiate the incident radiation in all directions. For the moment we consider just a Bravais lattice. Crystal structures with bases will be explained later. Sharp peaks will be observed only in directions and at wavelengths for which the rays scattered from all lattice points interfere constructively.

To find the condition for **constructive interference**, consider first just two scatterers, separated by a displacement vector \mathbf{d} :

**Figure 6.4**

Illustrating that the path difference for rays scattered from two points separated by \mathbf{d} is given by Eq. (6.3) or (6.4).

Let an X-ray be **incident** from very far away, along a direction $\hat{\mathbf{n}}$, with wavelength λ , and wavevector $\mathbf{k} = 2\pi\hat{\mathbf{n}}/\lambda$. A **scattered** ray will be observed in a direction $\hat{\mathbf{n}}'$ with same wavelength as the incident beam λ (in terms of photons this means that no energy has been lost in the scattering, i.e. that the

scattering is elastic) and wavevector $\mathbf{k}' = 2\pi\hat{\mathbf{n}}'/\lambda$. Constructive interference will be achieved provided that the path difference between the rays scattered by each of the two ions is an integral number of wavelengths. This path difference is just:

$$d \cos \theta + d \cos \theta' = \mathbf{d} \cdot (\hat{\mathbf{n}} - \hat{\mathbf{n}}').$$

The condition for constructive interference is thus:

$$\mathbf{d} \cdot (\hat{\mathbf{n}} - \hat{\mathbf{n}}') = m\lambda,$$

for integral m . Multiplying both sides by $2\pi/\lambda$ to get the phase difference yields a condition on the incident and scattered wave vectors for constructive interference: $\mathbf{d} \cdot (\mathbf{k} - \mathbf{k}') = 2\pi m$,

Next we consider not just two scatterers, but an array of scatterers, at the sites of a Bravais lattice. Since the lattice sites are displaced from one another by the Bravais lattice vectors \mathbf{R} , the condition that all scattered rays interfere constructively is that $\mathbf{d} \cdot (\mathbf{k} - \mathbf{k}') = 2\pi m$, holds simultaneously for all values of \mathbf{d} that are Bravais lattice vectors:

$$\mathbf{R} \cdot (\mathbf{k} - \mathbf{k}') = 2\pi m, \quad \text{for integral } m \text{ and all Bravais lattice vectors } \mathbf{R}.$$

LAUE LAW (1ST FORMULATION)

This can be written in the equivalent form

$$e^{i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{R}} = 1, \quad \text{for all Bravais lattice vectors } \mathbf{R}.$$

Comparing this condition with the definition of the reciprocal lattice $e^{i\mathbf{K} \cdot \mathbf{R}} = 1$ we arrive at the Laue condition that constructive interference between all scattered rays from all lattice points (Laue diffraction peak) will occur provided that the change in wavevector upon scattering, $\mathbf{K} = \mathbf{k}' - \mathbf{k}$, is a vector of the reciprocal lattice.

It is sometimes convenient to have an alternative formulation of the Laue condition, stated entirely in terms of the incident wave-vector \mathbf{k} . For this we need to combine the above Laue condition with the condition for elastic scattering (i.e. that \mathbf{k} and \mathbf{k}' have same magnitude). First note that because the reciprocal lattice is a Bravais lattice, if $\mathbf{k}' - \mathbf{k}$ is a reciprocal lattice vector, so is $\mathbf{k} - \mathbf{k}'$. Calling the latter vector \mathbf{K} , the condition that \mathbf{k} and \mathbf{k}' have the same magnitude (as required for elastic scattering) is $k = |\mathbf{k} - \mathbf{K}|$. Squaring both sides and dividing both sides by the magnitude of \mathbf{K} yields:

LAUE LAW (2ND FORMULATION)

$$\mathbf{k} \cdot \hat{\mathbf{K}} = \frac{1}{2}K;$$

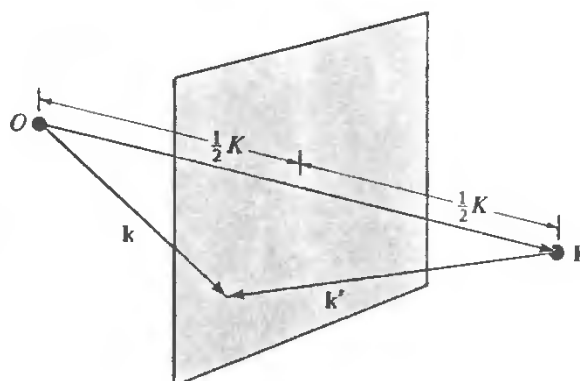
CONDITION FOR LAUE DIFFRACTION PEAK FOR ELASTIC SCATTERING OF WAVES IN A PERIODIC LATTICE

i.e. the component of the incident wave vector \mathbf{k} along the reciprocal lattice vector \mathbf{K} must be half the length of \mathbf{K} .

Thus an incident wave vector \mathbf{k} will satisfy the Laue condition for constructive interference between all scattered rays from all lattice points (Laue diffraction peak) if and only if the tip of the vector lies in a plane that is the perpendicular bisector of a line joining the origin of \mathbf{k} -space to a reciprocal lattice point \mathbf{K} . Such \mathbf{k} -space planes are called Bragg planes, each of which is associated with a particular diffraction peak. These planes are parallel to the family of direct lattice planes responsible for the peak in the Bragg formulation

Figure 6.5

The Laue condition. If the sum of \mathbf{k} and $-\mathbf{k}'$ is a vector \mathbf{K} , and if \mathbf{k} and \mathbf{k}' have the same length, then the tip of the vector \mathbf{k} is equidistant from the origin O and the tip of the vector \mathbf{K} , and therefore it lies in the plane bisecting the line joining the origin to the tip of \mathbf{K} .



This second formulation of the Laue condition provides a physical interpretation for the **1st Brillouin zone of the Bravais lattice**, defined as a Wigner-Seitz primitive cell in the reciprocal lattice. The WS PUC about a reciprocal lattice point (in this case the origin since we're considering the 1st Brillouin zone) is obtained by drawing reciprocal lattice vectors from the origin to all neighboring lattice points, bisecting each vector with a perpendicular plane and taking the smallest polyhedron containing the origin bounded by these planes. It is clear from the above Laue condition that the surface (boundaries) of this WSUC corresponds to all incident wavevectors giving diffraction peaks, i.e. **the walls of the reciprocal WSUC correspond to the Bragg planes**

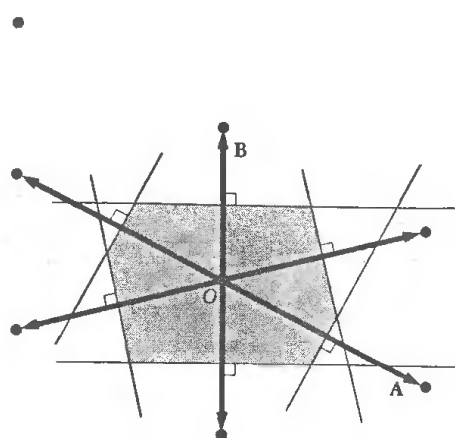


Figure 10 Construction of the first Brillouin zone for an oblique lattice in two dimensions. We first draw a number of vectors from O to nearby points in the reciprocal lattice. Next we construct lines perpendicular to these vectors at their mid-points. The smallest enclosed area is the first Brillouin zone.

EQUIVALENCE OF THE BRAGG AND VON LAUE FORMULATIONS AND APPEARANCE OF DIFFRACTION PATTERN

The equivalence of these two criteria for constructive interference of X-rays by a crystal follows from the relation between reciprocal lattice vectors and families of direct lattice planes. Suppose the incident and scattered wave vectors \mathbf{k} and \mathbf{k}' satisfy the Laue condition that $\mathbf{K} = \mathbf{k}' - \mathbf{k}$ be a reciprocal lattice vector. Because the incident and scattered waves have the same wavelength, \mathbf{k}' and \mathbf{k} have the same magnitudes. It follows that \mathbf{k}' and \mathbf{k} make the same angle θ with the plane perpendicular to \mathbf{K} :

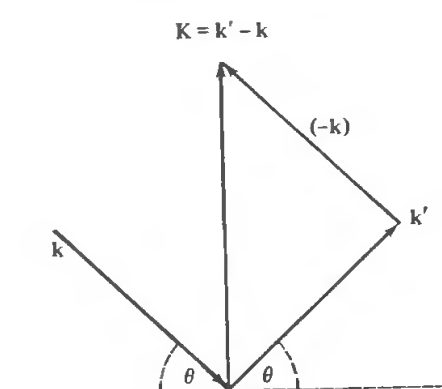


Figure 6.6

The plane of the paper contains the incident wave vector \mathbf{k} , the reflected wave vector \mathbf{k}' , and their difference \mathbf{K} satisfying the Laue condition. Since the scattering is elastic ($k' = k$), the direction of \mathbf{K} bisects the angle between \mathbf{k} and \mathbf{k}' . The dashed line is the intersection of the plane perpendicular to \mathbf{K} with the plane of the paper.

direct lattice planes perpendicular to the reciprocal lattice vector \mathbf{K} .

To demonstrate that this reflection satisfies Bragg's law, note that the vector \mathbf{K} is an integral multiple of the shortest reciprocal lattice vector \mathbf{K}_0 parallel to \mathbf{K} . As explained before, the magnitude of \mathbf{K}_0 is just $2\pi/d$, where d is the distance between successive planes in the family perpendicular to \mathbf{K}_0 or to \mathbf{K} . Thus:

$$K = \frac{2\pi n}{d}.$$

and it follows from fig 6.6 (from sine rule + trig identity $\sin(2\theta) = 2 \cos\theta \sin\theta$) that

, and thus:

$$K = 2k \sin \theta,$$

$$k \sin \theta = \frac{\pi n}{d}.$$

Since the above implies that the wavelength satisfies the Bragg law.

$$k = 2\pi/\lambda,$$

Thus the connection between Bragg's and Laue conditions for diffraction peaks is the following : a Laue diffraction peak corresponding to a change in wavevector given by the reciprocal lattice vector \mathbf{K} corresponds to a Bragg reflection from the family of direct lattice planes perpendicular to \mathbf{K} . The order,

n , of the Bragg reflection is just the length of K divided by the length of the shortest reciprocal lattice vector parallel to K (K_0).

Hence we can say in full glory that for a Bravais lattice each diffraction peak corresponds to a family of parallel lattice planes in the Bravais lattice (identified by Miller indices hkl), or to each possible reciprocal lattice vector. The connection between the two conditions for diffraction is expressed by the Miller indices: the Miller indices of a family of lattice planes are the coordinates of the shortest reciprocal lattice vector normal to that plane, with respect to a set of reciprocal primitive translation vectors. Thus a family of planes with Miller indices h,k,l is normal to the reciprocal lattice vector $K_0 =$

$$h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3.$$

Remember that for a given family of lattice planes you get many orders n of diffraction peaks, which correspond to different constructive reflections off the same family of lattice planes for different λ or θ which satisfy Bragg's law: $n\lambda = 2d \sin \theta$. Whereas there's no way to associate distinct Miller indices to each order of diffraction by looking at real space, in the reciprocal space condition for diffraction, the different orders correspond to the various members of the set of parallel reciprocal lattice vectors perpendicular to the family of lattice planes. In particular, the n th order peak from the plane family (hkl) corresponds to the reciprocal lattice vector $K = nK_0 = nh\vec{b}_1 + nk\vec{b}_2 + nl\vec{b}_3$ and is therefore associated with Miller indices (nh, nk, nl) (hkl have been minimized to the smallest three integers with no common factors as conventional)

HENCE EACH DIFFRACTION PEAK IN THE DIFFRACTION PATTERN, INCLUDING DIFFERENT ORDERS FROM THE SAME REAL FAMILY, IS ASSOCIATED WITH A DISTINCT RECIPROCAL LATTICE VECTOR

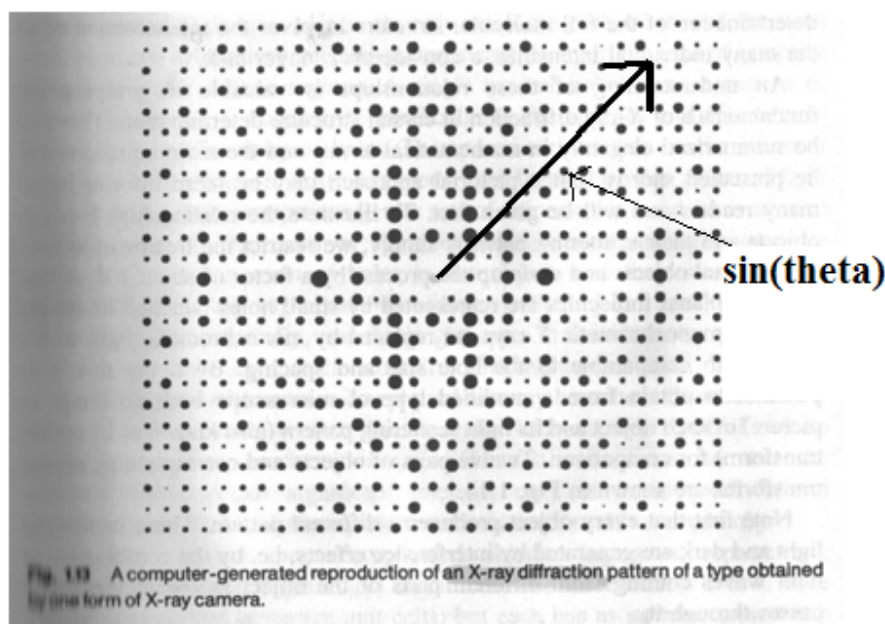
$K = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$ AND HENCE A DISTINCT SET OF MILLER INDICES hkl (not normalized to the lowest 3 integers)

RECIPROCAL LATTICE VECTOR $K = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$ (PROPERTY OF THE DIFFRACTING BRAVAIS LATTICE) \Downarrow OBSERVED DIFFRACTION SPOT hkl (opposite arrow not true, see systematic absences due to crystal structure)

NOTE: THE DIFFRACTION PATTERN IS REPRESENTED IN RECIPROCAL SPACE, BUT IT IS NOT THE RECIPROCAL LATTICE ITSELF (ONE IS 2D, THE OTHER IS 3D). The reciprocal lattice is a purely mathematical construction which is never observed in practice. In fact, the geometry of the diffraction pattern is the 2D projection of the 3D reciprocal lattice of the diffracting Bravais lattice, which means that the origin of the diffraction pattern has always indices $h=0, k=0, l=0$

Below is an example of a typical diffraction pattern in reciprocal k space for a monochromatic (fixed λ) x-ray beam on a single crystal which has been rotated through all angles θ . Note that this pattern represents the ideal case in which all successful combinations of d , θ and n are recorded as far as the 2D

space allows. The pattern is by no means complete, as there are many other diffraction spots which cannot be portrayed on the same plane as they would cause overlapping between spots with different indices, because 3D information is being compressed into a 2D record, and its measurements and interpretation would be impossible. What we want is each observed diffraction spot to correspond uniquely to a diffracted beam (reflection). Recording the whole of the diffraction pattern on one film is therefore impossible, and many 2D representations like the one shown below are necessary to get a complete representation of the 3D diffraction pattern (all reciprocal lattice points), even from a theoretical point of view: see experimental method section to see how the diffraction pattern is recorded and what it looks like in practice



This diffraction pattern has the following properties:

- Each diffraction spot is associated with a reciprocal lattice point, and hence a set of Miller Indices hkl .
- Some positions hkl in the diffraction pattern along the central vertical and horizontal axes corresponding to perfectly good K don't have a diffraction spot \diamond systematic absences due to presence of atoms in structure, which complicates above theory (developed only for Bravais lattices)
- The space group symmetry of the real crystal structure is revealed in various aspects of the appearance of the diffraction pattern, from which it is usually possible to choose the correct space group from the complete list of 230, or at least to narrow down the choice to a few possibilities
- At each point Bragg's law is satisfied. The three variables that can change are 1) the order n for a given family of lattice planes, and 2) distance d by considering different families of lattice planes (different ways of sectioning the lattice). For a given family, the different orders of diffraction

are probed by changing the Bragg angle θ . This is done by rotating the crystal (the direction of the x-ray beam is kept fixed). Note that for a given crystal orientation and beam direction, θ will be different for each family of planes

- The distance of each spot from the centre of the pattern is proportional to $\sin\theta$ and hence, from Bragg's law, to $1/d$ for some set of planes. This demonstrates mathematically the reciprocal (inverse) nature of the geometrical relationship between a crystal lattice and its diffraction pattern
- A key step in the process of finding the unit cell geometry ($a, b, c, \alpha, \beta, \gamma$) from the diffraction pattern is assigning the correct indices hkl to each of the observed reflections. There is no need to understand the geometry of the diffraction pattern to assign indices manually, as this is usually done automatically by the control software of the diffractometer. $a, b, c, \alpha, \beta, \gamma$ are therefore obtained effortlessly

Since the reciprocal lattice associated with a given Bravais lattice is far more easily visualized than the set of all possible planes into which the Bravais lattice can be resolved, the Laue condition for diffraction peaks is more simple to work with than the Bragg condition. We shall now apply the Laue condition to a description of three of the most important ways in which X-ray crystallographic analyses of real samples are performed, and to a discussion of how one can extract info not only about the underlying Bravais lattice, but also about the arrangement of ions in the unit cell of the crystal structure.

EXPERIMENTAL GEOMETRIES SUGGESTED BY THE LAUE CONDITION

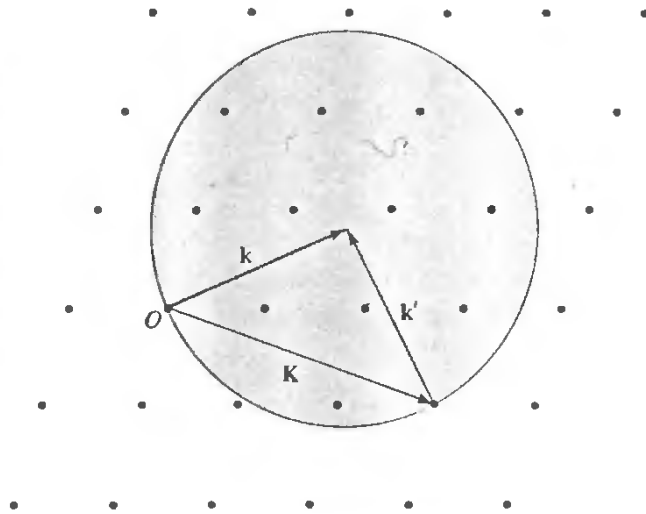
According to the Laue formulation, an incident wave vector \mathbf{k} will lead to a diffraction peak if and only if the tip of the wave vector lies on a \mathbf{k} -space Bragg plane. Since the set of all Bragg planes is a discrete family of planes, the Bragg planes together don't fill all 3D \mathbf{k} -space, and in general the tip of \mathbf{k} will not lie on a Bragg plane. Thus for a fixed incident wave-vector, i.e. for a fixed X-ray wavelength and fixed incident direction relative to the crystal axes, there will be in general no diffraction peaks at all. If one wishes to search experimentally for Bragg peaks one must therefore relax the constraint of fixed \mathbf{k} , either varying the magnitude of \mathbf{k} (i.e. varying the wavelength of the incident beam) or varying its direction (in practice, varying the orientation of the crystal wrt the incident direction)

EWALD CONSTRUCTION: A simple geometric construction due to Ewald is of great help in visualizing the various diffraction methods and in deducing the crystal structure from the observed diffraction peaks. Ewald sphere effectively represents Bragg law in reciprocal \mathbf{k} space. We draw in \mathbf{k} -space a sphere centered on the tip of the incident wave vector \mathbf{k} of radius k (so that it passes through the origin).

There will be some wave vector \mathbf{k}' satisfying the Laue condition if and only if some reciprocal lattice point (in addition to the origin) lies on the surface of the sphere, in which case there will be a Bragg reflection from the family of direct lattice planes perpendicular to that reciprocal lattice vector. A reflection corresponding to that reciprocal lattice point will be observed in the diffraction pattern

Figure 6.7

The Ewald construction. Given the incident wave vector \mathbf{k} , a sphere of radius k is drawn about the point \mathbf{k} . Diffraction peaks corresponding to reciprocal lattice vectors \mathbf{K} will be observed only if \mathbf{K} gives a reciprocal lattice point on the surface of the sphere. Such a reciprocal lattice vector is indicated in the figure, together with the wave vector \mathbf{k}' of the Bragg reflected ray.



In general a sphere in k -space with the origin on its surface will have no other reciprocal lattice points on its surface, and therefore the Ewald construction confirms our observation that for a general incident wave vector there will be no Bragg peaks. One can, however, ensure that some Bragg peaks will be produced (reciprocal lattice point on the sphere surface) by several techniques:

1. **The Laue Method (change λ):** One can continue to scatter from a single crystal of fixed orientation from a fixed incident direction $\hat{\mathbf{n}}$, but can search for Bragg peaks by using not a monochromatic X-ray beam, but one containing wavelengths from λ_1 up to λ_0 . The Ewald sphere will then expand into the region contained between the two spheres determined by $\mathbf{k}_0 = 2\pi\hat{\mathbf{n}}/\lambda_0$ and $\mathbf{k}_1 = 2\pi\hat{\mathbf{n}}/\lambda_1$, and Bragg peaks will be observed corresponding to any reciprocal lattice vectors lying within this region:

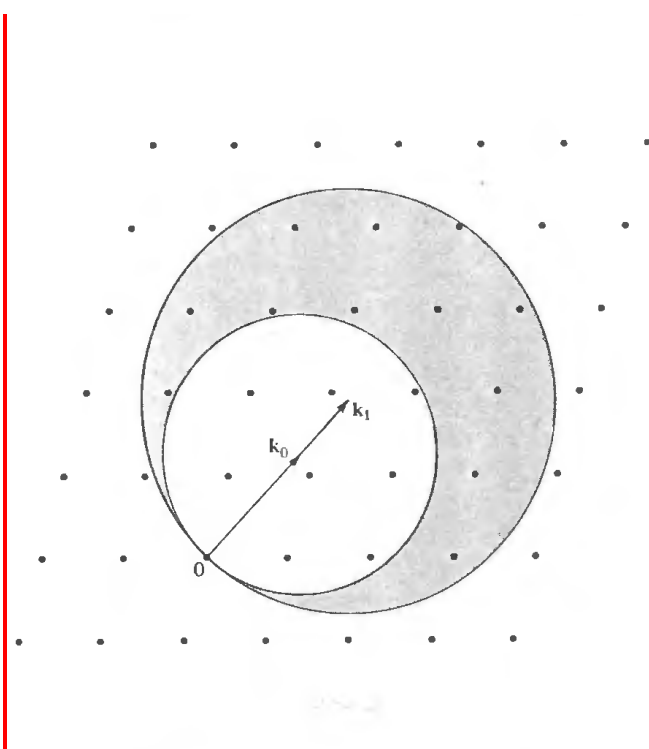


Figure 6.8

The Ewald construction for the Laue method. The crystal and incident X-ray direction are fixed, and a continuous range of wavelengths, corresponding to wave vectors between k_0 and k_1 in magnitude, is present. The Ewald spheres for all incident wave vectors fill the shaded region between the sphere centered on the tip of the vector k_0 and that centered on the tip of k_1 . Bragg peaks will be observed corresponding to all reciprocal lattice points lying within the shaded region. (For simplicity in illustration, the incident direction has been taken to lie in a lattice plane, and only reciprocal lattice points lying in that plane are shown.)

By making the spread in wavelengths sufficiently large, one can be sure of finding some reciprocal lattice points within the region, whereas by keeping it from getting too large, one can avoid too many Bragg reflections, thereby keeping the picture fairly simple.

The Laue method is probably best suited for determining the orientation of a single crystal specimen whose structure is known, since for example if the incident direction lies along a symmetry axis of the crystal, the pattern of spots produced by the Bragg reflected rays will have the same symmetry

- 2. The Rotating-Crystal Method (change θ):** This method uses monochromatic X rays, but allows the Bragg angle of incidence to vary. In practice the direction of the X-ray beam is kept fixed, and the orientation of the crystal varied instead. In the rotating crystal method the crystal is rotated about some fixed axis, and all the Bragg peaks that occur during the rotation are recorded on a film. As the crystal rotates, the reciprocal lattice it determines will rotate by the same amount about the same axis. Thus the Ewald sphere (which is determined by the fixed incident wave vector \mathbf{k}) is fixed in k -space, while the entire reciprocal lattice rotates about the axis of rotation of the crystal. During this rotation each reciprocal lattice point transverses a circle about the rotation axis, and a Bragg reflection occurs whenever this circle intersects the Ewald sphere:

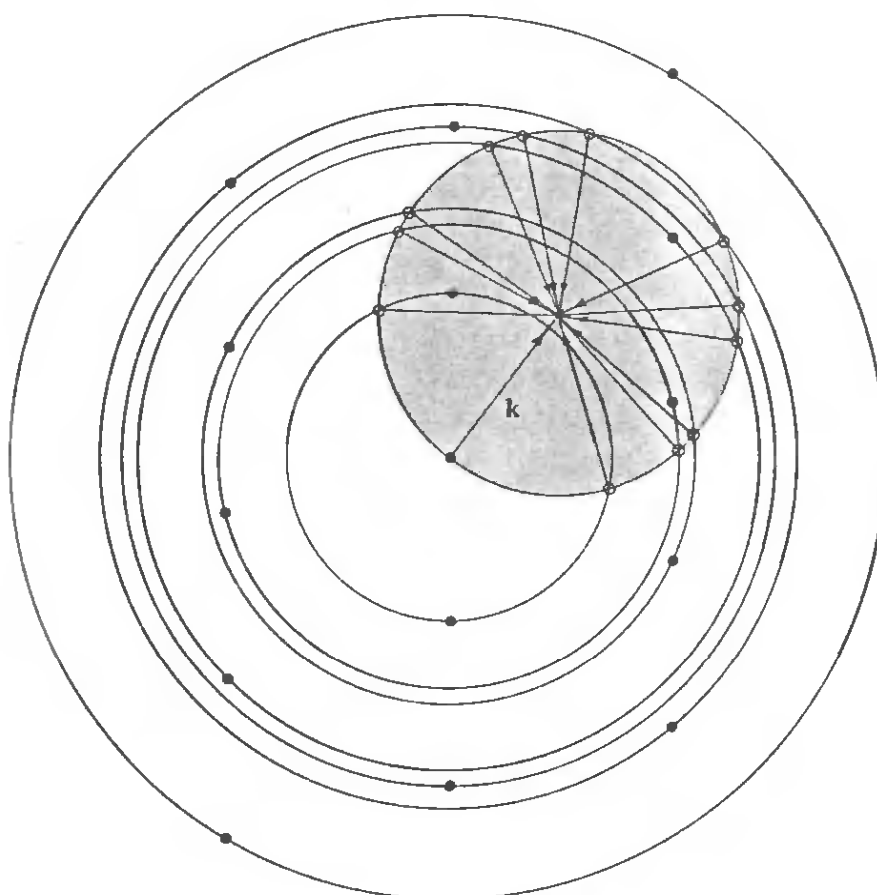


Figure 6.9

The Ewald construction for the rotating-crystal method. For simplicity a case is shown in which the incident wave vector lies in a lattice plane, and the axis of rotation is perpendicular to that plane. The concentric circles are the orbits swept out under the rotation by the reciprocal lattice vectors lying in the plane perpendicular to the axis containing k . Each intersection of such a circle with the Ewald sphere gives the wave vector of a Bragg reflected ray. (Additional Bragg reflected wave vectors associated with reciprocal lattice vectors in other planes are not shown.)

3. **The Powder or Debye-Scherrer Method (change θ):** This is equivalent to the rotating crystal method in which, in addition, the axis of rotation is varied over all possible orientations. In practice this isotropic averaging of the incident direction is achieved by using a fixed wavelength, and keeping the sample fixed, but using a polycrystalline sample or a powder, grains of which are still enormous on the atomic scale and therefore capable of diffracting X-rays. Because the crystal axes of the individual grains are randomly oriented, the diffraction

pattern produced by such a powder is what one would produce by combining the diffraction patterns for all possible orientations of a single crystal.

The Bragg reflections are now determined by fixing the incident k vector, and with it the Ewald Sphere, and allowing the reciprocal lattice to rotate through all possible angles about the origin, so that each reciprocal lattice vector K generates a sphere of radius K about the origin. Such a sphere will intersect the Ewald sphere in a circle provided that K is less than $2k$.

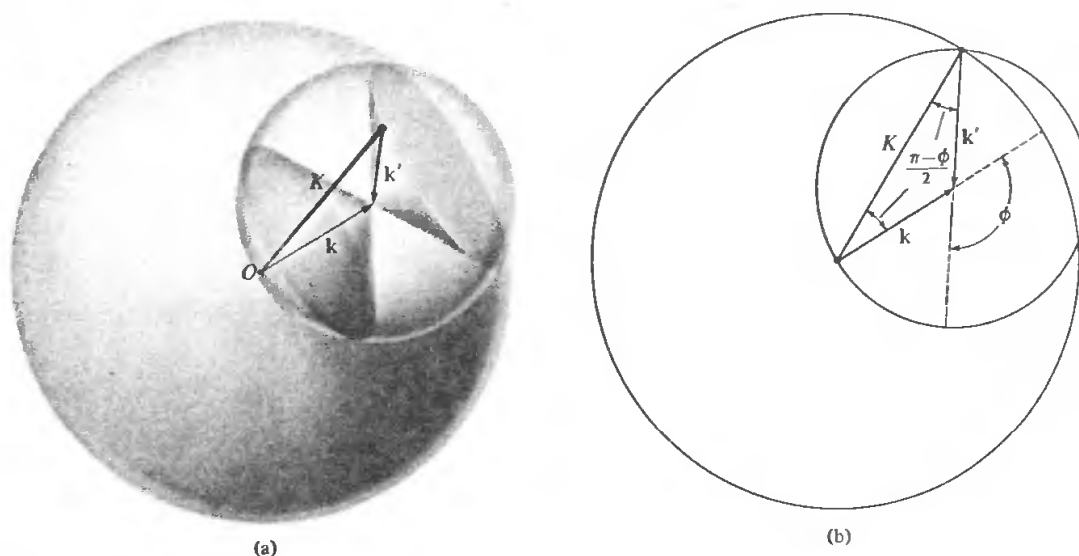


Figure 6.10

The Ewald construction for the powder method. (a) The Ewald sphere is the smaller sphere. It is centered on the tip of the incident wave vector k with radius k , so that the origin O is on its surface. The larger sphere is centered on the origin and has a radius K . The two spheres intersect in a circle (foreshortened to an ellipse). Bragg reflections will occur for any wave vector k' connecting any point on the circle of intersection to the tip of the vector k . The scattered rays therefore lie on the cone that opens in the direction opposite to k . (b) A plane section of (a), containing the incident wave vector. The triangle is isosceles, and thus $K = 2k \sin \frac{1}{2}\phi$.

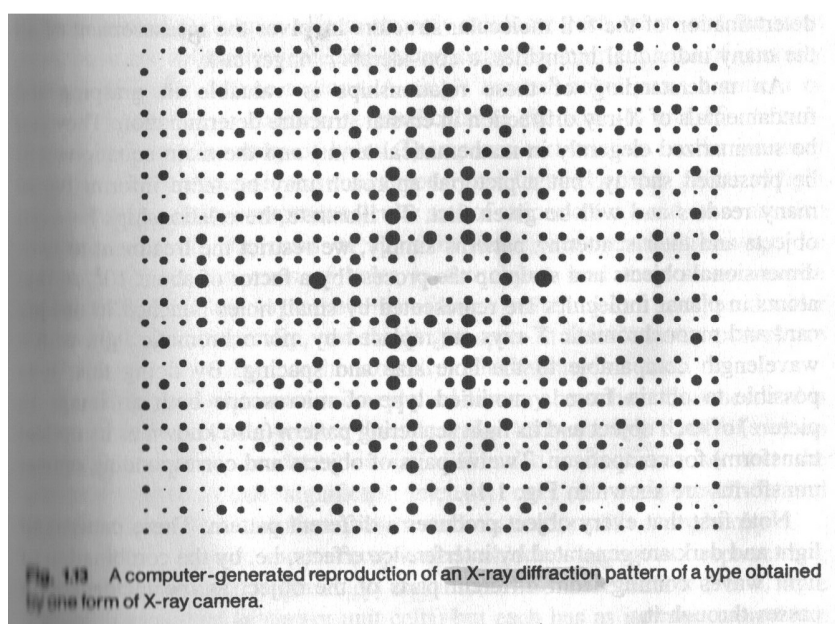
The vector joining any point on such a circle with the tip of the incident vector k is a wave-vector k' , for which scattered radiation will be observed. Thus each reciprocal lattice vector of length less than $2k$ generates a cone of scattered radiation at an angle ϕ to the forward direction, where:

$$K = 2k \sin \frac{1}{2}\phi.$$

By measuring the angles ϕ at which Bragg reflections are observed, one therefore learns the lengths of all reciprocal lattice vectors shorter than $2k$. Armed with this information, some facts about the macroscopic crystal symmetry, and the fact that the reciprocal lattice is a Bravais lattice, one can usually construct the reciprocal lattice itself.

1. APPEAREANCE OF DIFFRACTION PATTERNS

Below is an example of a pattern of scattered X-rays (diffraction pattern) produced by a single crystal. The diffraction pattern is always represented in reciprocal (k) space, related to real space of real crystal structure image by normal Fourier transform relations. The complete pattern is obtained by rotating the crystal in the X-ray beam. There are many different kinds of instruments for recording scattered X-rays, and they produce a variety of appearances, but in each case a good quality crystal always gives a pattern of spots of varied intensity. In the figure below, different intensities are represented by different sizes of the spots. On a photographic film, they would vary in their degree of blackness



The pattern of spots has three properties of interest, which correspond to three properties of the crystal structure.

1. The pattern has a particular geometry. The spots lie in certain positions which are clearly not random. Each spot is generated at the detector by an individual scattered X-ray beam travelling in a definite direction from the crystal. This pattern geometry is related to the reciprocal lattice and hence to the real Bravais lattice and unit cell geometry of the crystal structure and so can tell us the repeat distances between molecules.
2. Second the pattern has symmetry, not only in the regular arrangement of the spots but also in having equal intensities of spots which lie in symmetry related positions relative to the centre of the pattern. The pattern symmetry is closely related to the symmetry of the unit cell of the crystal structure (i.e. to the space group of the crystal structure). The above pattern has both vertical and horizontal reflection symmetries, and an inversion point at the centre.

3. Third, apart from this symmetry, there is no apparent relationship among the intensities of the individual spots. Some are very intense, while others are too weak to be seen. These intensities hold all the available information about the position of the atoms in the unit cell of the crystal structure (actually about the electron density distribution of the unit cell), because it is the relative atomic positions which through the combination of their individual interactions with the X-rays, generate different amplitudes for different directions of scattering.

Thus measurement of the geometry and symmetry of an X-ray scattering pattern provides information on the unit cell geometry and symmetry, while determination of the full molecular structure involves the measurement of all the many individual intensities, a considerably longer task. The analysis of x-ray diffraction patterns therefore play a fundamental role in crystal structure determination. To illustrate the relation between objects and scattering pattern simply, we restrict the treatment to 2D objects and scale up the process by a factor of about 10^4 , so that atoms in planar molecules are represented by small holes punched in opaque card and X-rays are replaced with monochromatic visible light with a λ comparable with the hole size and spacing. By doing this, it is possible to obtain with a microscope both an image of each object and its diffraction pattern in reciprocal space for comparison. Twelve pairs of objects and corresponding diffraction patterns are shown below:

14 The basis of the method

REAL IMAGE
(REAL SPACE)

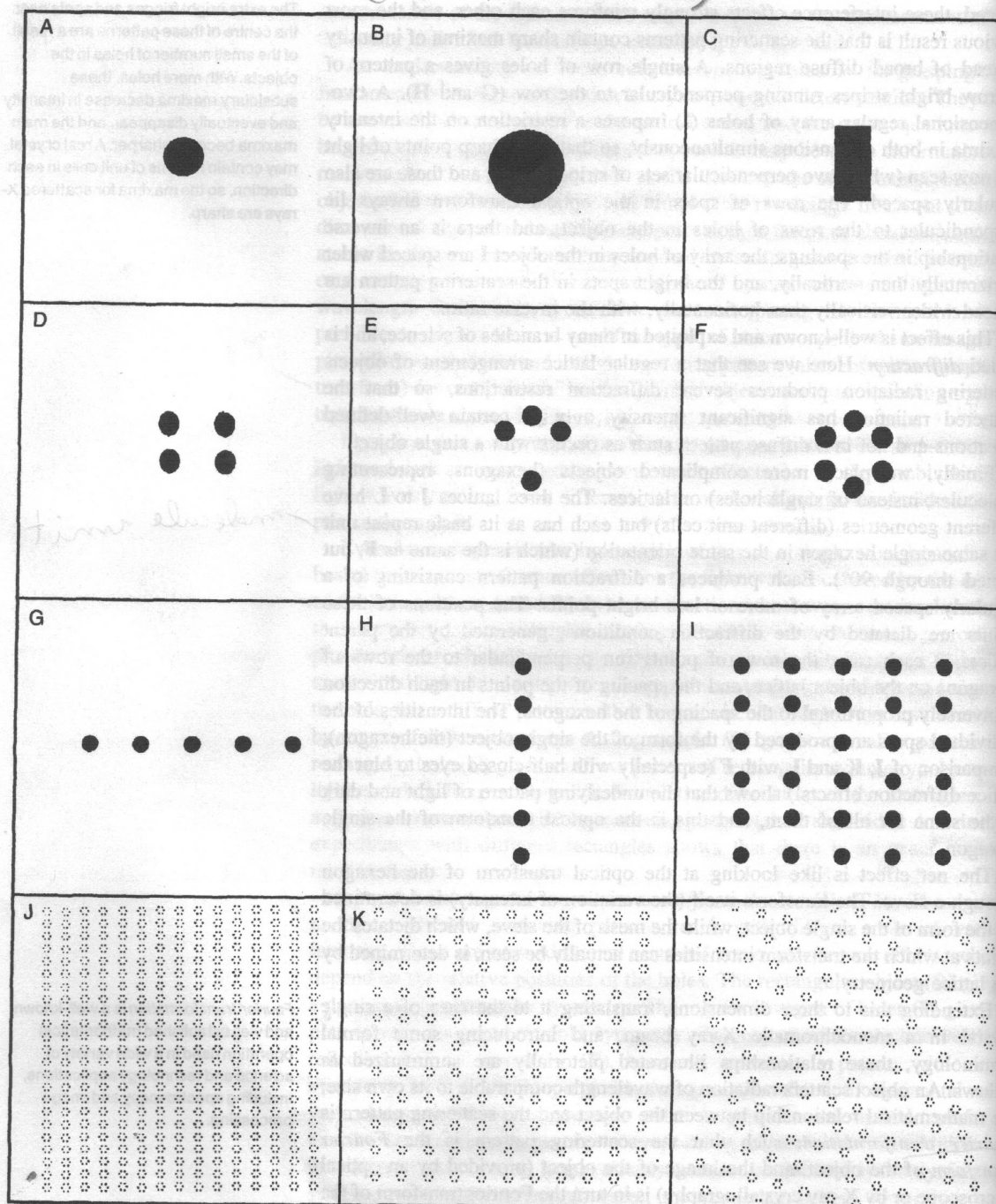
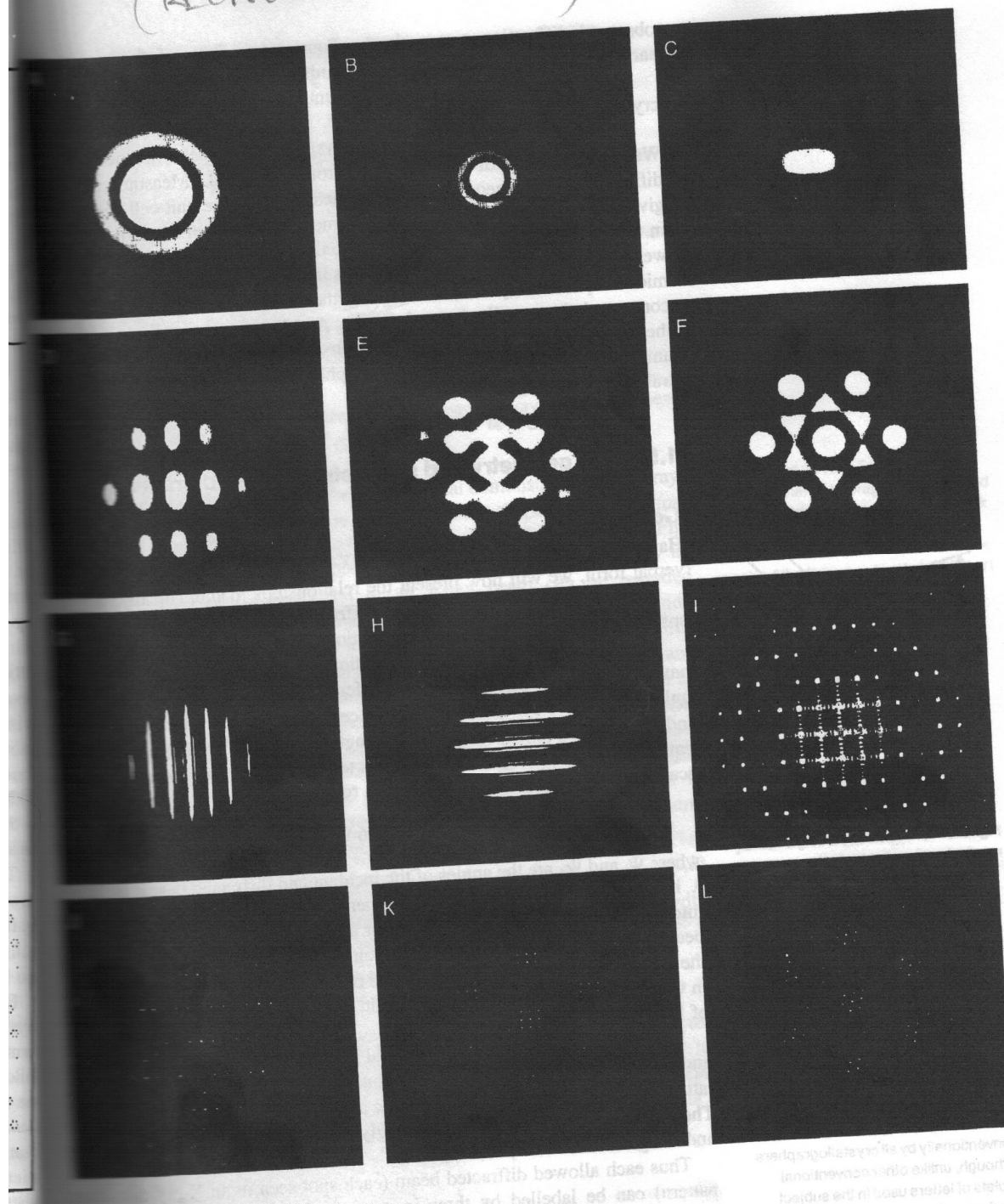


Fig. 114 A selection of objects and their optical scattering patterns. Each of the 12 objects on the left page has its scattering pattern in the corresponding position on the right page. The bottom row of objects is on a different scale; in the objects themselves, each hexagon has the same size as the individual hexagon in the second row. In the description in the text, the objects and their patterns are labelled from (A) to (C) in the top row, continuing to (L) at the end of the bottom row. These illustrations are taken from a very comprehensive compilation in *Atlas of Optical Transforms* by G. Harburn, C. A. Taylor and T. R. Welberry (G. Bell and Sons Ltd, London, 1975), with the permission of the authors.

DIFFRACTION PATTERN (RECIPROCAL SPACE)

Crystal structure determination 15



Note first that every object produces a different pattern. These patterns of light and dark are produced by interference effects, i.e. by combination of light waves coming from different parts of the object as the incident light passes through it

Even for a single circular hole (think of this as a single atom in an X-ray beam) there are interference effects for the light waves scattered by the edges of the hole (objects A and B). In some directions these waves are in phase and the scattering pattern is bright; in other directions, scattered waves are out of phase and cancel each other, so little or no net intensity is seen. Thus the transmitted light does not give a sharp pattern matching the shape and size of the hole, but a diffuse pattern with a central circular bright region surrounded by rings of lower intensity. A larger hole (B) gives a smaller pattern (Fourier reciprocal relation). A rectangular hole (C) gives a diffuse pattern of rectangular symmetry, also with light and dark fringes. Note that the relative dimensions of the rectangle (tall and narrow) are reversed in the scattering pattern (short and wide) (again due to the reciprocal relation). A series of experiments with different rectangles shows that there is an exactly inverse relationship.

Several holes together represent a single molecule (many atoms) (D to F). These give more complicated scattering patterns, each with diffuse areas of varying intensity. There are now additional scattered wave interference effects, which depend on the relative positions of the holes. The rectangular object (D) gives a pattern with rectangular symmetry. The regular hexagon of holes (F) gives a pattern with the same six-fold symmetry. The

object with only one vertical reflection line of symmetry (E), however, generates a pattern with extra symmetry: two mutually perpendicular lines of reflection, horizontal, vertical, intersecting in an inversion point.

In general each diffraction pattern has the same symmetry as the corresponding real object, with the addition of inversion symmetry if it's not already present. (and this may imply further symmetry elements as in this case). The scattering pattern never has less symmetry than the object. In 3D an equivalent rule applies, with the addition of an inversion centre to all scattering patterns.

Parts G to I show the effect of pure translation symmetry on the scattering of radiation by an object. Again extra interference effects take place for the light rays scattered from individual holes. Because the holes are regularly spaced, these interference effects strongly reinforce each other, and the most obvious result is that the scattering patterns contain sharp maxima of intensity instead of broad diffuse regions. A single row of holes gives a pattern of narrow stripes running perpendicular to the row (G and H). A two-dimensional regular array of holes (I) imposes a restriction on the intensity maxima in both dimensions simultaneously, so that only sharp points of light are now seen (where two perpendicular sets of stripes cross), and these are also regularly spaced. The rows of spots in the optical transform always lie perpendicular to the rows of holes in the object, and there is an inverse relationship in the spacings: the array of holes in the object I are spaced wider horizontally than vertically, and the bright spots in the scattering pattern are spaced wider vertically than horizontally, with the inverse ratio. Here we see that a regular lattice arrangement of objects scattering radiation produces severe diffraction restrictions, so that the scattered radiation has significant intensity only in certain well-defined directions and not in a diffuse pattern such as occurs with a single object

Finally, we place more complicated objects (hexagons, representing molecules, instead of single holes representing atoms) on lattices. The three lattices J to L have different geometries (different unit cells) but each has as its basic repeat unit (basis) the same single hexagon in the same orientation (which is the same as F, but turned through 90°). Each produces a diffraction pattern consisting of a regularly spaced array of more or less bright points. The positions of these points are dictated by the diffraction conditions, generated by the parent lattice in each case, the rows of points run perpendicular to the rows of hexagons on the object lattice, and the spacing of the points in each direction is inversely proportional to the spacing of the hexagons. The intensities of the individual spots are produced by the form of the single object (the hexagon). Comparison of J, K and L with F

shows that the underlying pattern of light and dark is the same for all of them, and this is the optical transform of the single hexagon

After looking at some examples of diffraction patterns, we'll see how the composition of the crystal structure affects diffracted intensities

6. INTENSITY OF DIFFRACTED WAVES AND RECOMBINATION CALCULATION

So far we've been discussing the appearance of a diffraction pattern purely in terms of constructive interference between waves scattered by a periodic array of lattice points (Bravais lattice), i.e. looking only at the relative phases of the waves diffracted by the crystal and using Bragg/ Laue laws. This is good in predicting the points where constructive interference occurs and therefore where diffraction spots should occur in the diffraction pattern (i.e. to explain the overall geometry of the diffraction pattern), because Laue's law predicts a diffraction spot for each reciprocal lattice point. However, considering only the underlying Bravais lattice of the crystal tells us nothing about the relative intensities of the diffraction spots. To do that we need to look at the atom composition of the basis associated with each lattice point, and hence at the full crystal structure. It turns out that for certain conditions, the scattered intensity for reciprocal point K can be zero even though K is a perfectly good reciprocal lattice point. We'll take the chance to summarise the full complete formalism for moving between the real crystal structure and the diffraction pattern in reciprocal space in terms of Fourier Transforms

The intensities of the diffraction pattern (reciprocal space) and the arrangement of atoms in the unit cell of the crystal structure (real space) are related to each other by Fourier transformation: the diffraction pattern is the direct Fourier Transform (FT) of the electron density (since electrons are the component of the atoms that scatter x-rays), and the electron density is itself the reverse Fourier Transform (FT^{-1}) of the diffraction pattern.

$$\text{electron density (real space)} \xrightleftharpoons[FT^{-1}]{FT} \text{diffraction pattern (reciprocal space)}$$

REPRESENTATION OF DIFFRACTED WAVES

The two numerical values associated with each reflection in a crystal diffraction pattern are the amplitude $|F|$ and the phase ϕ of the diffracted wave. The figure below shows two such waves; the amplitude $|F|$ is represented by the height of the wave, and the phase ϕ by the horizontal shift relative to some chosen origin.

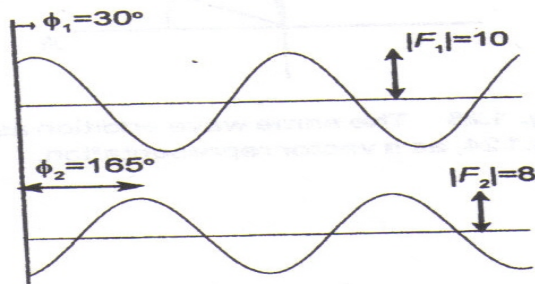


Fig. 1.21 Amplitudes and phases of two waves.

Another more compact way of representing the same waves is shown below. This is called a vector representation

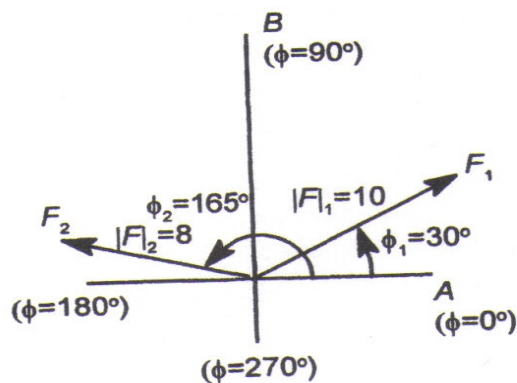


Fig. 1.22 The same two waves as in Fig. 1.21, represented as vectors.

Each wave is represented by an arrow with its tail at the centre of the diagram (the origin); the length of the arrow is proportional to the wave amplitude $|F|$, and the direction shows the phase ϕ , with a zero phase angle on the horizontal axis to the right and other angles ($0 \leq 2\pi$ radians) measured anti-clockwise from there. A vector \mathbf{F} has both magnitude $|F|$ and direction ϕ , like the arrows in the diagram. Instead of the two values of length and direction from the origin, each of the arrowhead positions could be specified by two coordinates on the horizontal (A) and vertical (B) axes. The mathematical relation between the vector (polar) and coordinate representations is in terms of the Pythagoras theorem:

$$|F|^2 = A^2 + B^2; \quad \tan \phi = B / A$$

$$A = |F| \cos \phi; \quad B = |F| \sin \phi$$

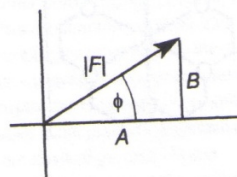


Fig. 1.23 The relationship between vector and coordinate representations.

An even more convenient notation for the diffracted wave is the complex notation, which mixes together the two components of the vector

$$F = A + iB$$

From the previous relation between the vector and coordinate representations, and using Euler's theorem, this becomes:

$$\begin{aligned} F &= |F| \cos\phi + i |F| \sin\phi \\ &= |F| (\cos\phi + i \sin\phi) \rightarrow \\ F &= |F| e^{i\phi} \end{aligned}$$

and we have the amplitude $|F|$ and phase ϕ of the diffracted wave represented by the one symbol F , a complex number.

Remember that each diffraction spot is labeled by its three Miller indices hkl , so for each reflection:

$F(hkl) = |F(hkl)| \exp[i\phi(hkl)]$ = STRUCTURE FACTOR of the diffracted wave with indices hkl (property of the diffracted wave). $|F|$ is the amplitude and ϕ the phase of the diffracted wave relative to the original beam incident on the crystal

ONE DIFFRACTED WAVE \diamond ONE DIFFRACTION SPOT @ $\underline{K} = h\underline{b}_1 + k\underline{b}_2 + l\underline{b}_3$

One final note: what is often measured in a diffraction pattern is the intensity of the diffracted waves rather than their amplitude. The relation is $I(hkl) \propto |F(hkl)|^2$

DIRECT FT IN TERMS OF CONTINUOUS ELECTRON DISTRIBUTION

Let's now look at how to do the direct Fourier Transform to get the diffracted waves from the electron density distribution in the unit cell. Note, in practice this is useless in experiments, since what we want to do is get the electron density from the diffraction pattern (i.e. the opposite process)

The diffraction pattern is the Fourier Transform of the electron density. Recall the definitions of the spatial FT of 3D function of position $f(\mathbf{r})$:

$$\begin{aligned} \tilde{f}(\vec{k}) &= \frac{1}{(2\pi)^{3/2}} \int f(\vec{r}) e^{-i\vec{k} \cdot \vec{r}} d^3\vec{r} \quad \text{DIRECT FT} \\ f(\vec{r}) &= \frac{1}{(2\pi)^{3/2}} \int \tilde{f}(\vec{k}) e^{i\vec{k} \cdot \vec{r}} d^3\vec{k} \quad \text{INVERSE FT} \end{aligned}$$

In our case the 3D function of position is the electron density in the crystal structure $\rho(r)$, and we can limit the integration to just one of the primitive unit cells. As said before, each diffraction spot is associated with a reciprocal lattice vector K and its Miller indices hkl , so the reciprocal variable k can in fact be restricted to:

$$\underline{K} = h\underline{b}_1 + k\underline{b}_2 + l\underline{b}_3 = \text{RECIPROCAL LATTICE POINT (b=reciprocal primitive vectors)}$$

The exponent in the FT can therefore be rewritten in an explicit form, using also atomic coordinates x,y,z for positions within the PUC in terms of the primitive vectors of the real Bravais lattice a (

$$\vec{r} = x\vec{a}_1 + y\vec{a}_2 + z\vec{a}_3):$$

$$\vec{K} \cdot \vec{r} = (h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3) \cdot (x\vec{a}_1 + y\vec{a}_2 + z\vec{a}_3) = 2\pi (hx + ky + lz)$$

NOTE: THIS ONLY WORKS WHEN APPLIED TO ONE PUC (NOT CUCs), SO THAT THE a s MUST BE PRIMITIVE VECTORS

The forward FT therefore is:

$$F(hkl) = \int_{\text{cell}} \rho(xyz) \exp[2\pi i(hx + ky + lz)] dV$$

The structure factor (amplitude and phase) for reflection hkl is therefore given by taking the value of the electron density (property of the real crystal structure) at each point in the unit cell $\rho(x,y,z)$, multiplying it by the complex number $\exp[2\pi i(hx + ky + lz)]$, and integrating these values over the whole primitive cell volume. Positions in the unit cell are measured from one corner (the origin) of the unit cell and the atomic coordinates x,y,z are in fractions of the corresponding crystal axes a,b,c

A physical interpretation can be given to this process of FT in terms of adding single diffracted waves together with their correct relative phases to get the total diffracted wave in one direction, but this is best understood in terms of scattering by individual atoms rather than a continuous electron distribution. This is explained later

This calculation can be carried out mathematically to mimic the observed experimental diffraction of X-rays by a crystal. It needs to be done for each possible reflection (each possible set of Miller indices for the different ways of sectioning the Bravais lattice in families of parallel lattice planes) and it produces a set of calculated structure factors, each with an amplitude $|F(hkl)|$ and a phase $\phi(hkl)$. In the experiments itself, of course, only the amplitudes are obtained by looking at the diffraction pattern (phase problem)

Since all the unit cells are identical, the total diffraction pattern of the crystal is just the Fourier transform of the contents of one unit cell multiplied by the number of unit cells in the single crystal, so there should be just a simple scale factor between the observed (whole crystal) and calculated (just one unit cell) sets of amplitudes.

DIRECT FT IN TERMS OF DISCRETE ATOMS

The equation in this form is not convenient for calculation, because it contains integration and a continuous function $p(xyz)$. Summation of a finite number of terms is easier (discrete FT). This can be achieved by expressing the electron density in terms of individual atoms. One atom scatters X-rays rather like a single circular hole scatters light passing through it, except that the scattering is by electrons throughout the atom and not just on its edges; this means that no outer rings of brightness are formed in the diffraction pattern in addition to the central one. In the forward direction ($2\theta = 0^\circ$) all the electrons scatter X-rays exactly in phase, but at all other angles there are partial destructive interference effects, so the intensity falls off as θ increases. The variation of intensity with angle (usually shown as a function of $(\sin\theta)/\lambda$ so that it is the same for X-rays of different λ for a given atom) is called the atomic form factor $f(\theta)$ and has the following general form:

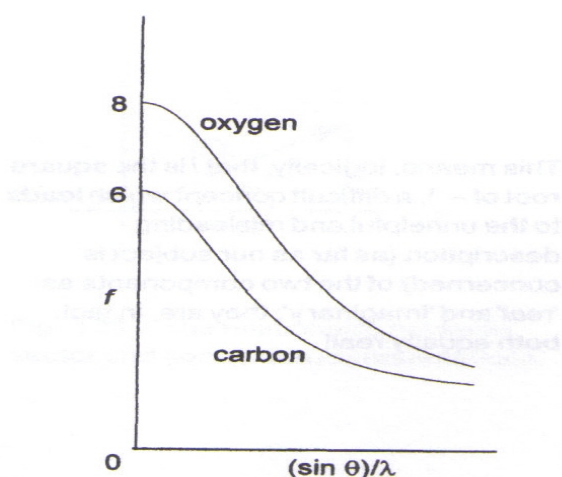


Fig. 1.26 X-ray atomic scattering factors for carbon and oxygen.

The inclusion of this form factor is necessary every time we want to work with individual atoms rather than the continuous electron distribution.

It is measured in units of electrons; $f(0)$, the scattering factor for zero deflection, is equal to the atomic number Z of the atom (number of electrons of the atom). This reflects the fact that X-rays interact with crystals through the atomic electrons and therefore the higher the Z of the atom, the higher the strength of interaction (i.e. the higher the amplitude of the atomic diffracted wave). The form factor is a unique property of each ion of a given element (regardless where it is placed in the PUC), and is obtained from QM calculations. The overall electron distribution in a solid as seen in x-ray diffraction is fairly close to that of the appropriate free atoms. This statement does not mean that the outermost or valence electrons are not redistributed in forming the solid; it means only that the x-ray reflection intensities are represented well by the free atom values of the form factors and are not very sensitive to small redistributions of the electrons.

Atoms in crystalline solids however are not stationary: they vibrate, to an extent which depends on the temperature, (thermal vibrations) and this effectively spreads out the atomic electron density and increases the interference effects. As a result, the form factor falls off more rapidly with increasing angle, and is not the same for all atoms of the same element, because they generally have different amounts of vibration unless they are symmetry-equivalent. For an atom which vibrates equally in all directions (isotropic vibration), the effect is to multiply the form factor by a term containing an isotropic displacement parameter U , which represents a mean square amplitude of vibration for the atom, a measure of how much it is vibrating:

$$f'(\theta) = f(\theta) \exp\left(-\frac{8\pi^2 U \sin^2 \theta}{\lambda^2}\right)$$

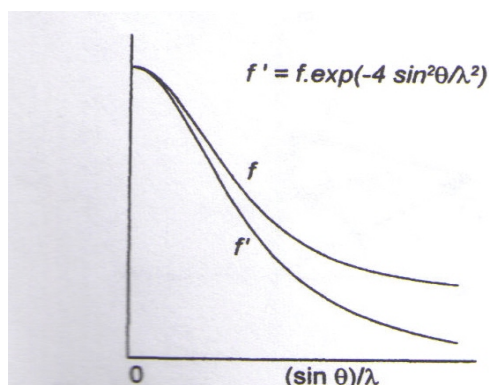


Fig. 1.27 The effect of atomic vibration on X-ray scattering factors; in this example, $8\pi^2 U = 4 \text{ \AA}^2$.

Note that U has units \AA^2 and the extra term has a value <1 . The larger the value of U , the more the curve falls off at higher Bragg angles θ .

FORWARD FOURIER TRANSFORM

With discrete atoms instead of a continuous electron density function, each atom with atomic

coordinates $\mathbf{r}_j = x_j \mathbf{a}_1 + y_j \mathbf{a}_2 + z_j \mathbf{a}_3$ (the \mathbf{a}_i are all primitive translation vectors) gives the following scattered wave:

$$F_j(hkl) = f_j'(\theta) \exp[2\pi i(hx_j + ky_j + lz_j)]$$

HKL(ATOMIC DIFFRACTED WAVE)

AMPLITUDE

PHASE

WAVE DIFFRACTED BY ATOM AT \mathbf{r}_j IN DIRECTION

For a given direction hkl , the amplitude of the atomic diffracted wave (net form factor) depends only on the type of atom, while the phase depends on the position of the atom in the primitive unit cell.

The forward Fourier transform therefore takes the form of an addition between waves scattered by individual atoms in the unit cell, which gives the total diffracted wave in the direction hkl :

$$F(hkl) = \sum_j F_j(hkl) = \sum_j f_j(\theta) \exp(-8\pi^2 U_j \sin^2 \theta / \lambda^2) \exp[2\pi i(hx_j + ky_j + lz_j)]$$

STRUCTURE

FACTOR (NET DIFFRACTED WAVE) IN DIRECTION HKL

The summation is made over all atoms of the primitive unit cell (actually all the atoms forming the basis associated with one lattice point), each of which has its appropriate atomic structure factor f_j (a function of the Bragg angle θ), a displacement parameter U_j , and atomic coordinates (x_j, y_j, z_j) relative to the unit cell origin. This summation must be carried out for every diffracted wave $F(hkl)$

Using discrete atoms helps to understand the physical origin of the FT relation between diffraction pattern and electron density. The above equation can in fact be understood in terms of the physical processes it represents. Every atom scatters X-rays falling on it (term $f_j(\theta) \exp(-8\pi^2 U_j \sin^2 \theta / \lambda^2)$). In any particular direction (hkl) , these separate scattered waves from each atom have different relative phases which depend on the relative positions of the atoms in the unit cell. (term $\exp(\vec{K} \cdot \vec{r}_j) = \exp[2\pi i(hx_j + ky_j + lz_j)]$ = PHASE OF WAVE DIFFRACTED BY ATOM J IN DIRECTION HKL), and the total diffracted wave in that direction ($F(hkl)$) is just the resultant sum (\sum_j) of the X-rays scattered by the individual atoms. The equation just represents the combination or addition of many waves each scattered by an individual atom in the primitive unit cell, added with their correct relative amplitudes and phases to give one resultant diffracted wave in each direction. The intensity of radiation in a given diffraction spot will depend on the extent to which the rays scattered from these atoms interfere constructively with one another. The graphical equivalent of this wave addition for two waves is shown below in both vector and wave representations:

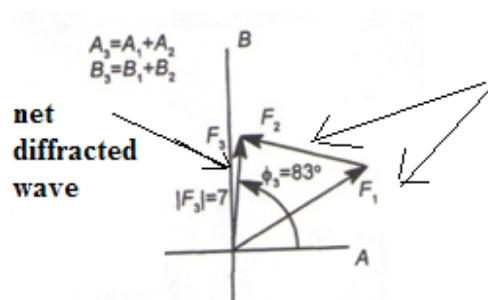


Fig. 1.25 The same wave addition as in Fig. 1.24, as a vector representation.

Atomic diffracted wave

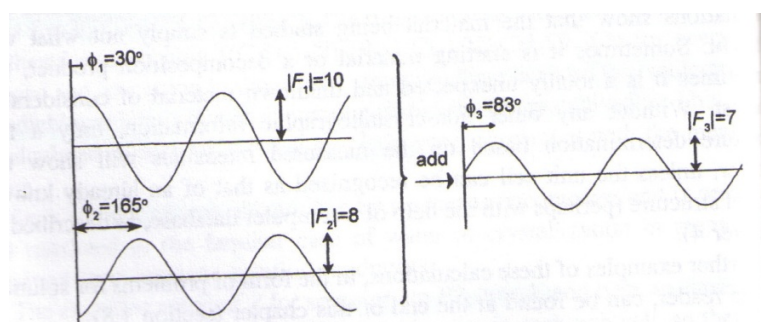


Fig. 1.24 Addition of two waves to give a resultant wave.

SYSTEMATIC ABSENCES


According to Laue's law (which was derived considering Bravais lattices only), Bragg reflections hkl can only occur when $\vec{K} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$ is a vector of the reciprocal lattice, (the geometry of the diffraction pattern is given by the 2D projection of the 3D reciprocal lattice). Hence in theory all hkl integer combinations are allowed in the diffraction pattern. This explains the overall geometry of the diffraction pattern

When we consider crystal structure, things get more complicated, because the presence of atoms affects the relative intensities of diffraction spots. It turns out that for some arrangements of atoms in the PUC of the crystal structure, certain diffraction spots corresponding to perfectly good reciprocal lattice vectors K (property of the diffracting Bravais lattice) disappear \diamond systematic absences (hkl with zero intensity). The indices hkl of systematic absences can be understood in terms of the above formula for structure factors. If, as a result of this addition of waves diffracted by the atoms in the PUC we have zero intensity at a spot hkl (structure factor $F(hkl)=0$), then we have a systematic absence. This occurs when the atoms of the unit cell are so arranged that there is complete destructive interference among all waves for the hkl direction in question. Exactly which combinations of hkl are allowed in the diffraction pattern, and hence the set of systematic absences, is a property of the space group of the crystal structure (since this destructive interference is a result of the symmetry properties of the crystal structure). The appearance of systematic absences in the diffraction pattern can tell us a great deal about the symmetry of the Bravais lattice, and hence help us identify the correct space group.


Consider for example this very simple crystal structure: a simple cubic Bravais lattice with a two-atom monoatomic basis consisting of $d_1=(000)$ and $d_2=(1/2,1/2,1/2)$ inside the PUC (like a bcc lattice). Since we're considering monoatomic crystal structures, form factors can be ignored, and only their relative phase will determine the appearance of missing orders. Therefore to predict missing orders we can take the structure factor to be simply $F(hkl) = \sum_j \exp[2\pi i(hx_j + ky_j + lz_j)]$.

So the structure factors associated with each Bragg reflection is:

$$F(hkl) = \sum_j \exp[2\pi i(hx_j + ky_j + lz_j)] = 1 + \exp(\pi i(h+k+l)) = 1 + (-1)^{h+k+l}$$



Atomic diffracted wave by atom 1



Atomic diffracted wave by atom 2

$F(hkl) = 0$ if $h+k+l$ is odd (systematic absence)

As a second example, take this crystal structure: simple cubic Bravais lattice with a two-point monoatomic basis at $d_1=(1/2,0,1/2)$; $d_2=(0,1/2,1/2)$ (like a fcc lattice):

$$F(hkl) = \sum_j \exp[2\pi i(hx_j + ky_j + lz_j)] = \exp(\pi i(h+l)) + \exp(\pi i(k+l)) = (-1)^{h+l} + (-1)^{k+l}$$

Systematic absence if h,k,l, are not all even or all odd

REVERSE FOURIER TRANSFORM (RECOMBINATIO CALCULATION)

The electron density distribution in the primitive unit cell (at position $\vec{r} = x\vec{a}_1 + y\vec{a}_2 + z\vec{a}_3$) is the reverse Fourier Transform (FT⁻¹) of the diffraction pattern. Because the diffraction pattern of a crystal consists of discrete reflections (diffraction spots) rather than a diffuse pattern, this Fourier transform is a summation, not an integral:

$$\rho(xyz) = \frac{1}{V} \sum_{h,k,l} F(hkl) \exp[-2\pi i(hx + ky + lz)]$$

$$\text{or } \rho(xyz) = \frac{1}{V} \sum_{h,k,l} |F(hkl)| \exp[i\phi(hkl)] \exp[-2\pi i(hx + ky + lz)]$$

The forward and reverse Fourier transforms differ in that one has a negative sign inside the exponential term. Remember that $F(hkl)$ is a complex number, containing both amplitude and phase information, as is shown explicitly in the second version. The term $1/V$ is necessary in order to give the correct units (form factors and structure factors have units of electrons, but electron density is electrons per Å³)

The summation is performed over all values of h,k,l (indices of diffracted waves), i.e. all the diffraction spots in the diffraction pattern contribute to the sum. In practice reflections are measured only to a certain maximum Bragg angle, but this is usually unimportant because the higher angle reflections are weaker and so contribute relatively little to the sums. The summation must be carried out for many different atomic coordinates x,y,z in order to show the variation of the electron density in the unit cell and hence locate the atoms where the electron density is concentrated in peaks.

As for the forward Fourier transform, this equation is best understood in terms of the (unachievable in practice) physical processes it represents. The image of the electron density $\rho(xyz)$, which originally generated the diffraction pattern, is obtained by adding together $\sum_{h,k,l}$ all the diffracted beams, with their correct amplitudes ($|F(hkl)|$) and phases ($\exp[i\phi(hkl)] \exp[-2\pi i(hx + ky + lz)]$); the correct relative phases here include the intrinsic phases of the diffracted waves themselves, relative to the

original incident beam ($\exp[i\phi(hkl)]$), and an extra phase shift appropriate to each geometrical position in the unit cell ($\exp[-2\pi i(hx + ky + lz)]$).

PHASE PROBLEM: This latter phase shift can be calculated as required, but the intrinsic phases $\phi(hkl)$ of the different reflections are unknown from the diffraction experiment, as all diffraction spots are recorded on the same observation plane with no info on which one arrived first etc... This means that it is not possible simply to calculate the reverse FT once the diffraction pattern has been measured. Here once again in the mathematical basis of the method we see the nature of the phase problem.