Diffraction I: Geometry

1 INTRODUCTION

After the preliminary survey of the physics of x-rays and the geometry of crystals, this chapter will fit the two together and discuss the phenomenon of x-ray diffraction, which is an interaction of the two. Historically, this is exactly the way this field of science developed. For many years, mineralogists and crystallographers had accumulated knowledge about crystals, chiefly by measurement of interfacial angles, chemical analysis, and determination of physical properties. There was little knowledge of interior structure, however, although some very shrewd guesses had been made, namely, that crystals were built up by periodic repetition of some unit, probably an atom or molecule, and that these units were situated some 1 or 2 Å apart. On the other hand, there were indications, but only indications, that x-rays might be electromagnetic waves about 1 or 2 Å in wavelength. In addition, the phenomenon of diffraction was well understood, and it was known that diffraction, as of visible light by a ruled grating, occurred whenever wave motion encountered a set of regularly spaced scattering objects, provided that the wavelength of the wave motion was of the same order of magnitude as the repeat distance between the scattering centers.

Such was the state of knowledge in 1912 when the German physicist von Laue (1879-1960) took up the problem. Stimulated by a discussion with P. P. Ewald of Ewald's doctoral dissertation (scattering of electromagnetic waves by an array of harmonic oscillators [1]), von Laue reasoned that, *if* crystals were composed of regularly spaced atoms which might act as scattering centers for x-rays, and *if* x-rays were electromagnetic waves of wavelength about equal to the interatomic distance in crystals, then it should be possible to diffract x-rays by means of crystals. Under his direction, Friedrich and Knipping conducted experiments to test this hypothesis: A crystal of copper sulfate was set up in the path of a narrow beam of x-rays and a photographic plate was arranged to record the presence of diffracted beams, if any. The second attempt was successful and showed without doubt that x-rays *were* diffracted by the crystal out of the primary beam to form a pattern of spots on the photographic plate [2]. These experiments proved, at one and the same time, the

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wave nature of x-rays and the periodicity of the arrangement of atoms within a crystal. Hindsight is always easy and these ideas appear quite simple now, when viewed from the vantage point of ninety years' development of the subject, but they were not at all obvious in 1912, and von Laue's hypothesis and its experimental verification must stand as a great intellectual achievement [G.11]

The account of these experiments was read with great interest by two English physicists, W. H. Bragg (1862-1942) and his son W. L. Bragg (1890-1971). The latter, although only a young student at the time-it was still the year 1912-successfully analyzed the Laue experiment and was able to express the necessary conditions for diffraction in a considerably simpler mathematical form than that used by von Laue [3]. He also attacked the problem of crystal structure with the new tool of x-ray diffraction and, in the following year, solved the structures of NaCl, KCl, KBr, and KI, all of which have the NaCl structure; these were the first complete crystal-structure determinations ever made [4]. The simpler structures of metals like iron and copper were not determined until later.

2 DIFFRACTION

Diffraction is due essentially to the existence of certain phase relations between two or more waves, and it is advisable, at the start, to get a clear notion of what is meant by phase relations. Consider a beam of x-rays, such as beam **1** in Fig. 1, proceeding from left to right. For convenience only, this beam is assumed to be plane-

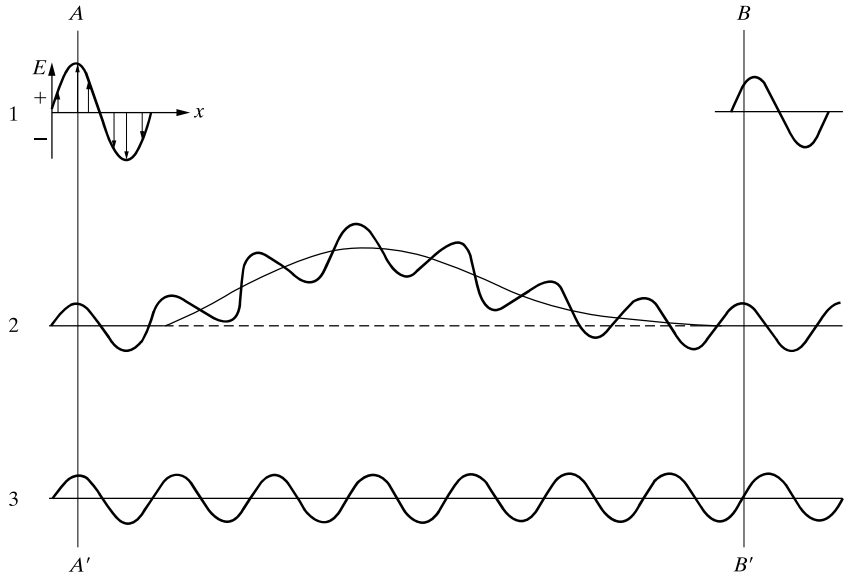

Figure 1 Effect of path difference on relative phase.

polarized so that the electric field vector **E** always lies in the plane of the drawing. Imagine this beam to be composed of two equal parts, ray **2** and ray **3**, each of half the amplitude of beam **1**. These two rays, on the wave front AA', are said to be completely *in phase* or in step; i.e., their electric-field vectors have the same magnitude and direction at the same instant at any point x measured along the direction of propagation of the wave. A *wave front* is a surface perpendicular to this direction of propagation.

Now consider an imaginary experiment, in which ray **3** is allowed to continue in a straight line but ray **2** is diverted by some means into a curved path before rejoining ray **3**. What is the situation on the wave front BB' where both rays are proceeding in the original direction? On this front, the electric vector of ray **2** has its maximum value at the instant shown, but that of ray **3** is zero. The two rays are therefore *out of phase*. Adding these two imaginary components of the beam together, produces the form of beam **1** shown in the upper right of the drawing. If the amplitudes of rays **2** and **3** are each 1 unit, then the amplitude of beam **1** at the left is 2 units and that of beam **1** at the right is 1.4 units, if a sinusoidal variation of **E** with x is assumed.

Two conclusions may be drawn from this illustration:

1. Differences in the length of the path traveled lead to differences in phase.
2. The introduction of phase differences produces a change in amplitude.

The greater the path difference, the greater the difference in phase, since the path difference, measured in wavelengths, exactly equals the phase difference, also measured in wavelengths. If the diverted path of ray **2** in Fig. 1 were a quarter wavelength longer than shown, the phase difference would be a half wavelength. The two rays would then be completely out of phase on the wave front BB' and beyond, and they would therefore annul each other, since at any point their electric vectors would be either both zero or of the same magnitude and opposite in direction. If the difference in path length were made three quarters of a wavelength greater than shown, the two rays would be one complete wavelength out of phase, a condition indistinguishable from being completely in phase since in both cases the two waves would combine to form a beam of amplitude 2 units, just like the original beam. Thus, two rays are completely in phase whenever their path lengths differ either by zero or by a whole number of wavelengths.

Differences in the path length of various rays arise quite naturally when considering how a crystal diffracts x-rays. Figure 2 shows a section of a crystal, its atoms arranged on a set of parallel planes *A, B, C, D*, ..., normal to the plane of the drawing and spaced a distance d' apart. Assume that a beam of perfectly parallel, perfectly monochromatic x-rays of wavelength λ is incident on this crystal at an angle θ, called the Bragg angle, where θ is measured between the incident beam and the particular crystal planes under consideration.

Whether this incident beam of x-rays will be diffracted by the crystal and, if so, under what conditions, are the questions central to this chapter. *A diffracted beam may be defined as a beam composed of a large number of scattered rays mutually reinforcing one another*. Diffraction is, therefore, essentially a scattering phenome-

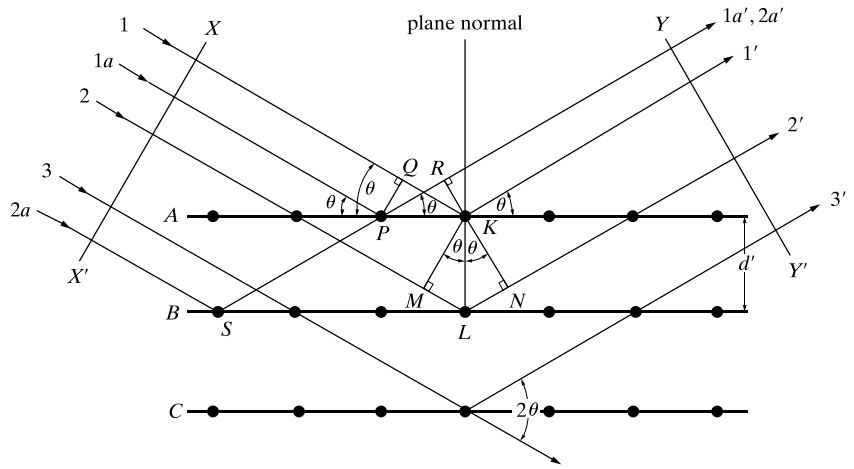

Figure 2 Diffraction of x-rays by a crystal.

non and not one involving any "new" kind of interaction between x-rays and atoms. Atoms scatter incident x-rays in all directions and the following paragraphs demonstrate that in some of these directions the scattered beams will be completely in phase and so reinforce each other to form diffracted beams.

For the particular conditions described by Fig. 2, the only diffracted beam formed is that shown, namely one making an exit angle θ with respect to the diffraction planes[1] equal to the angle θ of incidence. This will be shown, first, for one plane of atoms and, second, for all the atoms making up the crystal. Consider rays **1** and **1a** in the incident beam; they strike atoms K and P in the first plane of atoms and are scattered in all directions. Only in the directions $1'$ and $1a'$, however, are these scattered beams completely in phase and so capable of reinforcing one another; they do so because the difference in their length of path between the wave fronts XX' and YY' is equal to

$$QK - PR = PK\cos\theta - PK\cos\theta = 0.$$

Similarly, the rays scattered by all the atoms in the first plane in a direction parallel to $1'$ are in phase and add their contributions to the diffracted beam. This will be true of all the planes separately, and it remains to find the condition for reinforcement of rays scattered by atoms in different planes. Rays **1** and **2**, for example, are scattered by atoms K and L, and the path difference for rays **1***K*1′ and **2***L*2′ is

$$ML + LN = d'\sin\theta + d'\sin\theta.$$

[1] Note that these angles are defined differently in x-ray diffraction and in general optics. In the latter, the angles of incidence and reflection are the angles which the incident and reflected beams make with the *normal* to the reflecting surface.

This is also the path difference for the overlapping rays scattered by S and P in the direction shown, since in this direction there is no path difference between rays scattered by S and L or P and K. Scattered rays $1'$ and $2'$ will be completely in phase if this path difference is equal to a whole number n of wavelengths, or if

$$n\lambda = 2d' \sin \theta. \tag{1}$$

This relation was first formulated by W. L. Bragg and is known as Bragg's law. It states the essential condition which must be met if diffraction is to occur. n is called the order of diffraction; it may take on any integral value consistent with $\sin\theta$ not exceeding unity and is equal to the number of wavelengths in the path difference between rays scattered by *adjacent* planes. Therefore, for fixed values of λ and d', there may be several angles of incidence $\theta_1, \theta_2, \theta_3, \ldots$ at which diffraction may occur, corresponding to $n = 1, 2, 3, \ldots$. In a first-order reflection ($n = 1$), the scattered rays $1'$ and $2'$ of Fig. 2 would differ in length of path (and in phase) by one wavelength, rays $1'$ and $3'$ by two wavelengths, rays $1'$ and $4'$ by three wavelengths, and so on throughout the crystal. The rays scattered by all the atoms in all the planes are therefore completely in phase and reinforce one another (constructive interference) to form a diffracted beam in the direction shown. In all other directions of space the scattered beams are out of phase and annul one another (destructive interference). The diffracted beam is rather strong compared to the sum of all the rays scattered in the same direction, simply because of the reinforcement which occurs,[2] but is extremely weak compared to the incident beam since the atoms of a crystal scatter only a small fraction of the energy incident on them.

It is helpful to distinguish three scattering modes:

1. By atoms arranged randomly in space, as in a monatomic gas. This scattering occurs in *all* directions and is weak. Intensities add.
2. By atoms arranged periodically in space, as in a perfect crystal:
   a) In a very few directions, those satisfying Bragg's law, the scattering is strong and is called diffraction. Amplitudes add.

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[2] If the scattering atoms were not arranged in a regular, periodic fashion but in some independent manner, then the rays scattered by them would have a random phase relationship to one another. In other words, there would be an equal probability of the phase difference between any two scattered rays having any value between zero and one wavelength. Neither constructive nor destructive interference takes place under these conditions, and the intensity of the beam scattered in a particular direction is simply *the sum of the intensities* of all the rays scattered in that direction. If there are N scattered rays each of amplitude A and therefore of intensity A^2 in arbitrary units, then the intensity of the scattered beam is NA^2. On the other hand, if the rays are scattered by the atoms of a crystal in a direction satisfying Bragg's law, then they are all in phase and the amplitude of the scattered beam is *the sum of the amplitudes* of the scattered rays. The total amplitude is then N times the amplitude A of each scattered ray, or NA. The intensity of the scattered beam is therefore N^2A^2, or N times as large as if reinforcement had not occurred. Since N is very large for the scattering of x-rays from even a small bit of crystal, ($N = 1.1 \times 10^{19}$ atoms for 1 mg of iron), the role of reinforcement in producing a strong diffracted beam is considerable.

b) In most directions, those not satisfying Bragg's law, there is no scattering because the scattered rays cancel one another.

At first glance, the diffraction of x-rays by crystals and the reflection of visible light by mirrors appear very similar, since in both phenomena the angle of incidence is equal to the angle of reflection. It seems that the planes of atoms act as little mirrors which "reflect" the x-rays. Diffraction and reflection, however, differ fundamentally in at least three aspects:

1. The diffracted beam from a crystal is built up of rays scattered by all the atoms of the crystal which lie in the path of the incident beam. The reflection of visible light takes place in a thin surface layer only.
2. The diffraction of monochromatic x-rays takes place only at those particular angles of incidence which satisfy Bragg's law. The reflection of visible light takes place at any angle of incidence.
3. The reflection of visible light by a good mirror is almost 100 percent efficient. The intensity of a diffracted x-ray beam is extremely small compared to that of the incident beam.

Despite these differences, the terms "reflecting planes" and "reflected beams" are often used when diffracting planes and diffracted beams are described. This is common usage and, from now on, these terms will appear without quotation marks but with the tacit understanding that diffraction is meant and not reflection.[3] Also, always remember it is the constructive interference of scattering from the atoms which produces diffracted intensity. Lack of understanding of what the commonly used term "diffracting planes" represents, can lead to errors.

To sum up, diffraction is essentially a scattering phenomenon in which a large number of atoms cooperate. Since the atoms are arranged periodically on a lattice, the rays scattered by them have definite phase relations between them; these phase relations are such that destructive interference occurs in most directions of scattering, but in a few directions constructive interference takes place and diffracted beams are formed. Strictly speaking, for interference to occur, the interacting waves must be superimposed physically (i.e., waves 1a′ and 2a′ in Fig. 2), but given the cloud-like distribution of electrons around the nucleus of each scattering atom, the relatively large depth of penetration of the x-ray beam and the large number of scattering events which typically occur in a sample, the requirement for physical superposition is normally left implicit in treatments of diffraction. The two essentials are a wave motion capable of interference (x-rays) and a set of periodically arranged scattering centers (the atoms of a crystal).

[3] For the sake of completeness, it should be mentioned that x-rays *can* be totally reflected by a solid surface, just as visible light is by a mirror, but only at very small angles of incidence (below about one degree). X-ray reflectivity is a powerful technique for studying surfaces and internal interfaces which lie in the vicinity of the surface [5]. Commercial instrumentation ranging from high resolution diffractometers to dedicated x-ray reflectometers are available, and the theory and experimental methods are summarized elsewhere [6, 7].

3 BRAGG'S LAW

Two geometrical facts are worth remembering: (1) The incident beam, the normal to the diffraction plane, and the diffracted beam are always coplanar. (2) The angle between the diffracted beam and the transmitted beam is always 2θ. This is known as the diffraction angle, and it is this angle, rather than θ, which is usually measured experimentally.

As previously stated, diffraction in general occurs only when the wavelength of the wave motion is of the same order of magnitude as the repeat distance between scattering centers. This requirement follows from Bragg's law. Since $\sin\theta$ cannot exceed unity,

$$\frac{n\lambda}{2d'} = \sin\theta < 1. \tag{2}$$

Therefore, $n\lambda$ must be less than $2d'$. For diffraction, the smallest value of n is 1. ($n = 0$ corresponds to the beam diffracted in the same direction as the transmitted beam. It cannot be observed.) Therefore the condition for diffraction at any observable angle 2θ is

$$\lambda < 2d'. \tag{3}$$

For most sets of crystal planes d' is of the order of 3 Å or less, which means that λ cannot exceed about 6 Å. A crystal could not possibly diffract ultraviolet radiation, measuring for example, of wavelength about 500 Å. On the other hand, if λ is very small the diffraction angles requires very specialized equipment.

Bragg's law may be written in the form

$$\lambda = 2\frac{d'}{n}\sin\theta. \tag{4}$$

Since the coefficient of λ is now unity, a reflection of any order can be considered as a first-order reflection from planes, real or fictitious, spaced at a distance $1/n$ of the previous spacing. This turns out to be a real convenience, so that $d = d'/n$ and

$$\lambda = 2d\sin\theta. \tag{5}$$

This form will be used throughout this book.

This usage is illustrated by Fig. 3. Consider the second-order 100 reflection[4] shown in (a) for a simple cubic substance. Since it is second-order, the path difference ABC between rays scattered by adjacent (100), say i and $i + 1$ planes must be two whole wavelengths.

[4] This means the reflection from the (100) planes. Conventionally, the Miller indices of a diffraction plane *hkl*, written without parentheses, stand for the diffracted beam from the plane (*hkl*).

In the simple cubic structure all of the lattice points are on one of the (100) and are separated by $d = a/(1^2 + 0 + 0)^{0.5} = a$. If there were scatterers on the dotted plane midway between the ith and (i+1)th planes (Fig. 3b),[5] they would scatter one wavelength out of phase with the atoms on the ith and (i+1)th planes. The ith, (i+1/2)th and (i+1)th planes are, therefore, positions of equal phase in the diffracted beam. This periodicity, that for second order 100 diffraction, is $a/2$ and is indicated by d_{200}. Note that the formula for d-spacings using $h = 2$, $k = 0$ and $l = 0$ yields $d_{200} = a/2$. Similar considerations hold for diffraction of the third, fourth, etc., orders of (100), i.e., the, 300, 400, etc. reflections. In general, nth-order diffraction from (hkl) with spacing d' may be considered as a first-order diffraction from ($nh\ nk\ nl$) with spacing $d = d'/n$. Note that this convention accords with the definition of Miller indices since ($nh\ nk\ nl$) are the Miller indices of planes parallel to (hkl) but with $1/n$th the spacing of the latter. The presence or absence of atoms at different positions within the unit cell, such as on the (i+1/2)th plane in Fig. 3, has a profound effect on the diffracted intensity observed for different reflections.

4 LAUE'S EQUATIONS

Bragg's equation describes diffraction in terms of a scalar equation. Crystals are, in general, three-dimensional entities, and, for greatest generality, equations developed to describe the diffracted beam directions need to be expressed in terms of vectors.

Consider a one-dimensional array of scatterers spaced a apart (Fig. 4). Let the incident beam direction be denoted $\mathbf{S}_0$ and make an angle α_o with the line of scatterers, and define the diffracted beam direction as $\mathbf{S}$. In order for the path difference to be an integral multiple of wavelengths $h\lambda$, the angle α which $\mathbf{S}$ makes with the line of scatterers must satisfy:

$$a(\cos\alpha - \cos\alpha_0) = h\lambda. \tag{6a}$$

This equation is satisfied for a series of cones with axes concentric with the row of scatterers and with semi-apex angle of α.

Next consider a two-dimensional network of scatterers with spacing a along one axis and b along the second axis. If the angles $\mathbf{S}_0$ and $\mathbf{S}$ make with the rows spaced b apart are β_0 and β, respectively, a second equation must be simultaneously be satisfied in order for constructive interference to occur:

$$b(\cos\beta - \cos\beta_0) = k\lambda, \tag{6b}$$

where k is an integer. Similarly, a third condition arises when one considers a three-dimensional array of scatterers with spacing c in the third dimension:

[5] The dotted plane in Fig. 3 *is* occupied by atoms in the face-centered and body-centered Bravais lattices.

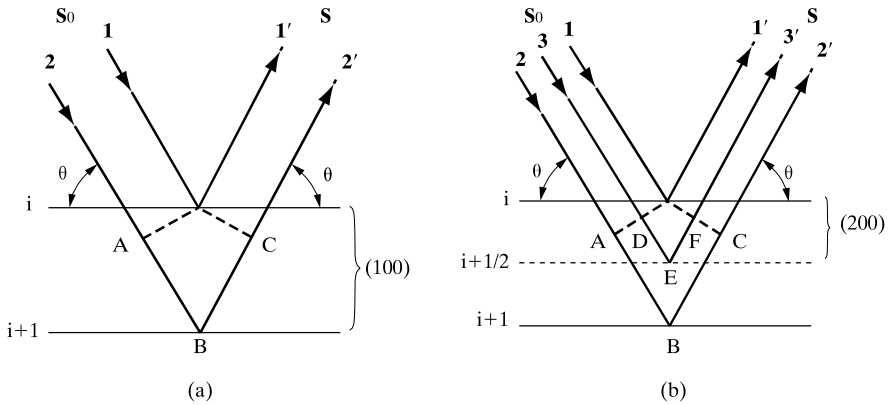


Figure 3 Equivalence of (a) a second-order 100 reflection and (b) a first-order 200 reflection. The incident and diffracted beam directions are $\mathbf{S}_0$ and $\mathbf{S}$, respectively, and the ith, (i+1/2)th and (i+1)th planes are labeled.

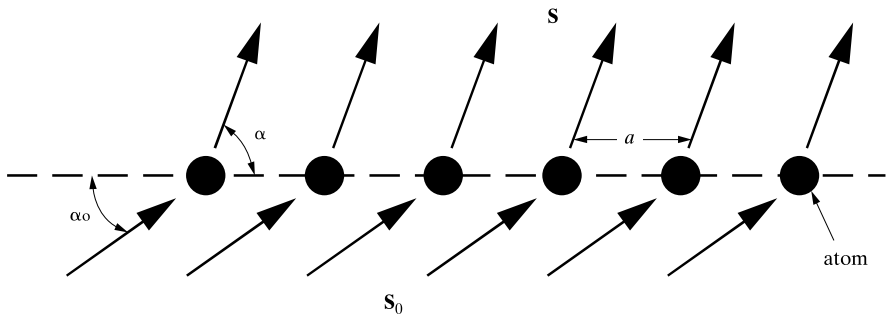


Figure 4 One-dimensional array of scatters with periodicity a, beam $\mathbf{S}_0$ incident at angle α_o and diffracted beam $\mathbf{S}$ at angle α.

$$c(\cos\gamma - \cos\gamma_0) = l\lambda, \tag{6c}$$

where l is an integer. The Eq. 6 are collectively known as Laue's Equations and emphasize the three-dimensional nature of diffraction. Generally, Bragg's law is more convenient to use for numerical purposes, and, as will be shown in the following section, the three-dimensionality of diffraction is more easily seen using the reciprocal lattice.

5 RECIPROCAL LATTICE AND DIFFRACTION

The reciprocal lattice can also be used to determine the geometric conditions for diffraction. First, in the direct space lattice consider the interference between scattering from two lattice points O and A (Fig. 5). Point O is at the origin of the lattice, and point A is located relative to O by vector $\mathbf{OA} = p\mathbf{a}_1 + q\mathbf{a}_2 + r\mathbf{a}_3$, where *r, q,* and *p* are integers. Note that *p, q,* and *r* must be integers since both O and A are lattice points. For x-rays of wavelength λ, incident beam $\mathbf{S}_0$ and diffracted beam $\mathbf{S}$, the path difference δ for x-rays scattered from O and A is

$$\begin{aligned}\delta &= \mathrm{uA} + \mathrm{Av} \\ &= \mathrm{Om} + \mathrm{On} \\ &= \mathrm{S}_0 \cdot \mathrm{OA} + (-\mathrm{S}) \cdot \mathrm{OA} \\ &= -\mathrm{OA} \cdot (\mathrm{S} - \mathrm{S}_0), \end{aligned} \tag{7}$$

and the corresponding phase difference ϕ (in radians) is

$$\phi = 2\pi\delta/\lambda = -\frac{2\pi(\mathrm{S} - \mathrm{S}_0) \cdot \mathrm{OA}}{\lambda} = -2\pi \cdot \mathscr{S} \cdot \mathbf{OA} \tag{8}$$

where $\mathbf{S}$ and $\mathbf{S}_0$ are unit vectors and $\mathscr{S} = (\mathrm{S} - \mathrm{S}_0/\lambda)$ and is termed the scattering vector. Note that $\mathscr{S}$ is in units of $\mathrm{\AA}^{-1}$. Implicit in this treatment is that vectors $\mathbf{a}_i$ are for a primitive unit cell for whatever crystal system is being considered. Giving the vectors $\mathbf{a}'_i$ in terms of a non-primitive unit cell has important consequences, however, which are beyond the scope of this chapter.

The link to the reciprocal latttice comes through defining $\mathscr{S}$ as a vector in that space, i.e., by letting

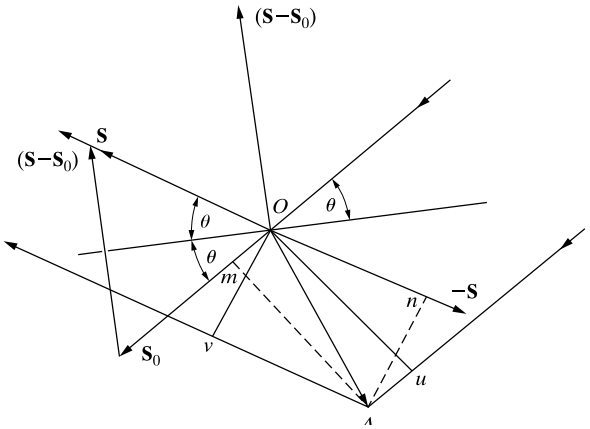


Figure 5 X-ray scattering by atoms at *O* and *A*. After Guinier [G.13].

$$\mathscr{H} = h'\mathbf{b_1} + k'\mathbf{b_2} + l'\mathbf{b_3}, \tag{9}$$

and noting that h', k' and l' have no special significance and are continuously variable. After substituting the vector expressions for $\mathscr{H}$ and **OA** in Eq. 8, the result is

$$\begin{aligned}\phi &= -2\pi(h'\mathbf{b_1} + k'\mathbf{b_2} + l'\mathbf{b_3}) \cdot (p\mathbf{a_1} + q\mathbf{a_2} + r\mathbf{a_3}) \\ &= -2\pi(h'p + k'q + l'r).\end{aligned} \tag{10}$$

In order for diffraction to occur, ϕ must be an integral multiple of 2π; in order for this to be true simultaneously for many *p, q, r* (i.e., for many different scattering sites) h', k' and l' must be integers which will now be written *h, k* and *l*. Thus, $\mathscr{H}$ or $(\mathrm{S} - \mathrm{S}_0/\lambda)$ must start and end on points of the reciprocal lattice.

The conditions for diffraction can be represented graphically in reciprocal space using the Ewald sphere construction [2.3]. While the reciprocal lattice of a three dimensional crystal is also three dimensional, a convenient plane through reciprocal space normally is plotted; the reciprocal lattice plane perpendicular to $\mathbf{b}_3$ and through the origin of the reciprocal lattice is used to illustrate the Ewald sphere construction. The first step in plotting the Ewald sphere representation of diffraction is to construct the reciprocal lattice in question. Next one plots S_0/λ parallel to the incident beam direction, giving it length $1/\lambda$ Å^{-1} and terminating it at the origin of the reciprocal lattice. The sphere centered at the origin of vector S_0/λ and with radius $1/\lambda$ represents the locus of possible **S** for wavelength λ and is termed the Ewald sphere. In order for diffraction to be observed (i.e., for Bragg's law to be satisfied), **S** and, hence, $\mathscr{H}$ must end on a reciprocal lattice point. This means that $\mathscr{H}$ is parallel to the normal of (*hkl*)and has magnitude $1/d_{\mathrm{hkl}}$, and Bragg's law (or the Laue equations) can be derived directly from the Ewald sphere construction. Perhaps the most important point to remember is that the Ewald sphere must intersect a reciprocal lattice point *hkl* for diffraction from (*hkl*) to be observed.

An important property of the transformation from the direct space lattice to the reciprocal lattice (and the reverse transformation) is that vectors in one lattice are physically parallel to their counterpart in the other lattice. For example, the direction from the Ewald sphere center to the reciprocal lattice point *hkl* on the sphere is **S** and defines the direction along which the diffracted beam $\mathbf{S}_{\mathrm{hkl}}$ is observed. In direct space the parallel vector, also written as **S**, defines the diffracted beam direction. It is possible for certain $\mathbf{S}_0$ to produce two or more diffracted beams simultaneously, but, given the wavelengths of x-rays used in diffractometry and the lattice parameters of crystals, this possibility is unlikely. [6]

[6] In the case of electrons used in the transmission electron microscope, wavelengths are at least an order of magnitude smaller than those of x-rays used in diffractometry. The result, as will be seen in Sec. 9, is that multiple diffracted beams are the rule rather than the exception for electron diffraction.

There is another way of viewing the direct space to reciprocal space transformation. Note that the incident and diffracted beams $\mathbf{S}_0$ and $\mathbf{S}$ each consist of many parallel rays displaced from each other in space. Then the transformation to reciprocal space can be viewed as mapping all parallel rays to a single point, just as was seen for the periodic "planar" arrays of lattice point being mapped onto a single point in the reciprocal lattice. This aspect of the reciprocal lattice is covered in more detail in Sec. 9.

An example of the Ewald sphere construction is shown in Fig. 6 for a simple orthorhombic crystal with lattice parameters $a_1 = 2.0$ Å, $a_2 = 1.0$ Å and $a_3 = 3.0$ Å. The corresponding magnitudes of the reciprocal lattice vectors are $b_1 = 0.5$ Å^{-1}, $b_2 = 1.0$ Å^{-1} and $b_3 = 0.33$ Å^{-1}, and Fig. 6 shows the reciprocal lattice adjacent to the direct space lattice. If the orthorhombic crystal is oriented for 100 diffraction with Cu $K\alpha$ radiation ($\lambda = 1.54$ Å), $\mathbf{S}_0$ must make an angle of 22.6° with (100). This is shown for $\mathbf{S}_0$ in the plane of the paper, i.e., this $\mathbf{S}_0$ makes an angle of 22.6° with $\mathbf{a}_2$, and the resulting $\mathbf{S}$ makes the same angle with $-\mathbf{a}_2$.

Remember that the Bragg angle for 100 is not equal to that for 010 or 001 in the orthorhombic system. The lengths of S_0/λ and S/λ are (1.54 Å)$^{-1}$ = 0.649 Å^{-1}, and S_0/λ and the corresponding Ewald sphere are shown to scale and in the correct orientation in the reciprocal lattice. The Ewald sphere intersects the reciprocal lattice point (1,0,0), and 100 diffraction will occur. Note that the direction of the diffracted beam in reciprocal space is parallel to that in direct space and that the angle between $\mathbf{S}_0$ and $\mathbf{S}$ in Fig. 6 is 2θ. One should also note that the symmetry present in the direct space lattice must also be reflected in the reciprocal lattice.

Rotation of $\mathbf{S}_0$ about $\mathbf{a}_3$ can be used to orient the crystal to diffract from other $\langle h00 \rangle$.[7] In order to orient the crystal shown in Fig. 6 for 200 diffraction, i.e., second order 100 diffraction, $\mathbf{S}_0$ must rotate 27.75° from its orientation in Fig. 6 toward $\mathbf{a}_1$. This rotation brings the Ewald sphere into contact with the 200 reciprocal lattice point. Similarly, $\mathbf{S}_0$ must rotate 45.2° counterclockwise from the orientation pictured in Fig. 6 in order to produce $\bar{1}00$ diffraction.

The possible diffraction beam directions for a given crystal can also be determined using the Ewald sphere construction. Consider the reciprocal lattice for the simple orthorhombic crystal shown in Fig. 6. Remembering that the condition for diffraction from (*hkl*) is that the Ewald sphere intersects the *hkl* reciprocal lattice point, the Ewald sphere can be rotated about the origin of the reciprocal lattice, through all possible orientations, to determine which *hkl* reflections are possible (Fig. 7). The result is the *limiting sphere* centered on the origin of the reciprocal lattice and with radius $2/\lambda$. All the diffracted beams corresponding to the reciprocal lattice points lying within or on the limiting sphere can be excited for the proper crystal orientation. One advantage of using the reciprocal lattice to determine

[7] Users of x-ray diffraction often speak of rotating the incident beam while keeping the crystal orientation fixed. For practical reasons, it is actually the crystal which is rotated and the incident x-ray beam which remains stationary.

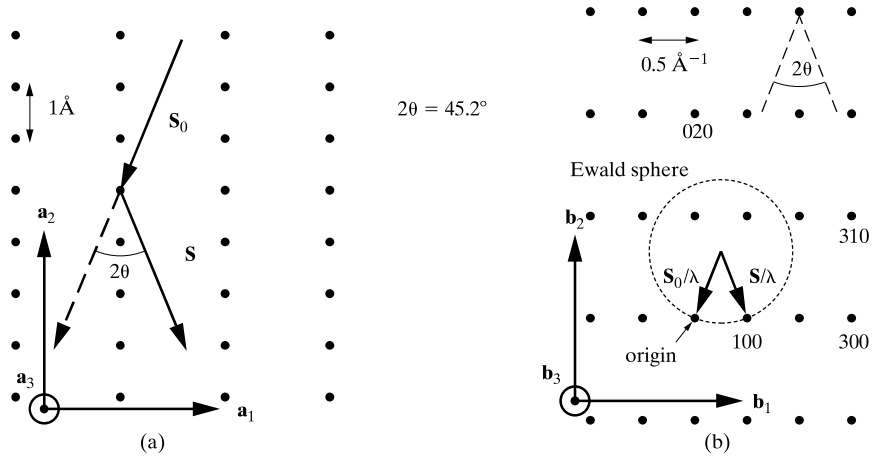


Figure 6 (a) Direct space lattice for a simple orthorhombic crystal and (b) the corresponding reciprocal space lattice and Ewald sphere for Cu $K\alpha$ radiation. The orientation of the incident beam $\mathbf{S}_0$ is such that 100 diffraction occurs, i.e., (100) are oriented to satisfy Bragg's law and the reciprocal lattice point 100 is on the Ewald sphere.

which diffracted beams are possible is that the directions of $\mathbf{S}$ and $\mathbf{S}_0$ are obvious; this is not the case for the numerical approach described in the previous paragraphs of this section. When numerical values of the Bragg angle are required, however, it is advantageous to use Bragg's law directly.

6 DIFFRACTION DIRECTIONS

What determines the possible directions, i.e., the possible angles 2θ, in which a given crystal can diffract a beam of monochromatic x-rays? Referring to Fig. 3, the various diffraction angles $2\theta_1, 2\theta_2, 2\theta_3, \ldots$ can be obtained from the (100) planes by using a beam incident at the correct angle $\theta_1, \theta_2, \theta_3, \ldots$ and producing first-, second-, third-, ... order reflections. But diffraction can also be produced by the (110) planes, the (111) planes, the (213) planes, and so on. A general relation is needed which will predict the diffraction angle for *any* set of planes. This relation is obtained by combining Bragg's law and the plane-spacing equation applicable to the particular crystal involved.

For example, if the crystal is cubic, then

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

and

$$\frac{1}{d^2} = \frac{(h^2 + k^2 + l^2)}{a^2}.$$

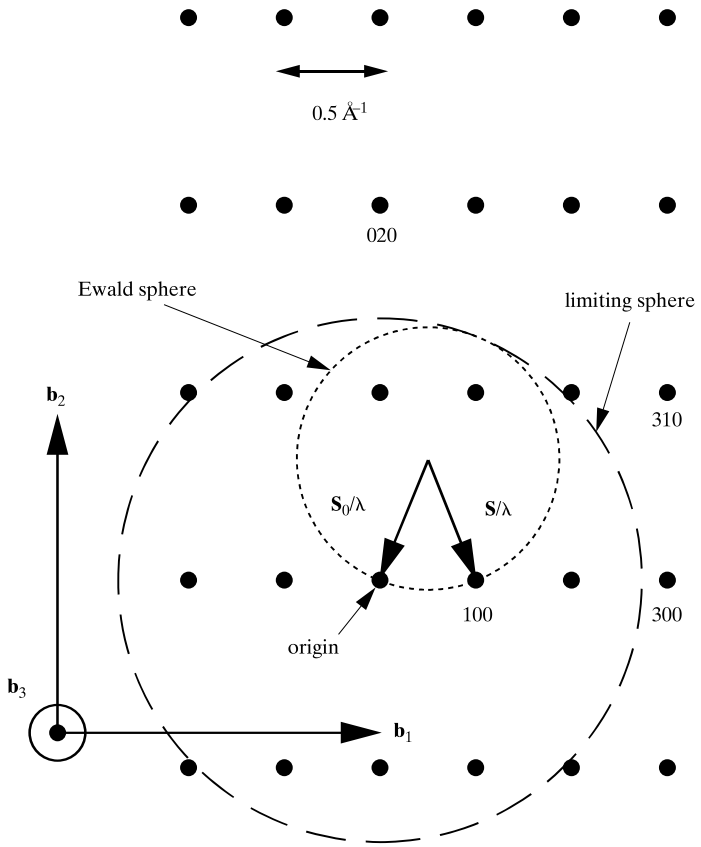


Figure 7 Illustration of the limiting sphere. The Ewald sphere and reciprocal lattice of Fig. 6 are shown for reference; $\mathbf{S}_0$ is shown oriented for 100 diffraction. Diffraction from 100, 200, 110, 010, etc. is possible for this crystal and x-ray wavelength; 300, 210, etc, diffraction cannot be observed.

Combining these equations rearranging terms produces

$$\sin^2\theta = \frac{\lambda^2}{4a^2}(h^2 + k^2 + l^2). \tag{11}$$

This equation predicts, for a particular incident wavelength λ and a particular cubic crystal of unit cell size a, all the possible Bragg angles at which diffraction can occur from the planes (hkl). For (110) planes, for example, Eq. (11) becomes

$$\sin^2\theta_{110} = \frac{\lambda^2}{2a^2}.$$

If the crystal is tetragonal, with axes a and c, then the corresponding general equation is

$$\sin^2\theta = \frac{\lambda^2}{4}\left(\frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}\right) \tag{12}$$

and similar equations can readily be obtained for the other crystal systems.

These examples show that the directions in which a beam of given wavelength is diffracted by a given set of lattice planes are determined by the crystal system to which the crystal belongs and its lattice parameters. In short, *diffraction directions are determined solely by the shape and size of the unit cell.* This is an important point and so is its converse: all that can be determined about an unknown crystal by measurements of the *directions* of diffracted beams are the shape and size of its unit cell. *Intensities* of diffracted beams are determined by the positions of the atoms within the unit cell, and it follows that intensities must be measured if any information at all is to be obtained about atom positions. For many crystals, there are particular atomic arrangements which reduce the intensities of some diffracted beams to zero. In such a case, there is simply no diffracted beam at the angle predicted by an equation of the type of Eqs. (11) and (12). It is in this sense that equations of this kind predict all *possible* iffracted beams.

7 X-RAY SPECTROSCOPY

Experimentally, Bragg's law can be applied in two ways. By using x-rays of known wavelength and measuring θ, the spacing d of various planes in a crystal are determined: this is *structure analysis* and is the subject, in one way or another, of the greater part of this book. Alternatively, a crystal with planes of known spacing d can be used to measure θ, and thus determine the wavelength λ of the radiation used: this is *x-ray spectroscopy*.

The essential features of an x-ray spectrometer [8] are shown in Fig. 8. X-rays from the tube T are incident on a crystal C which may be set at any desired angle to the incident beam by rotation about an axis through O, the center of the spectrometer circle. D is a detector which measures the intensity of the diffracted x-rays; it can also be rotated about O and set at any desired angular position. The crystal is usually cut or cleaved so that a particular set of diffracting planes of known spacing

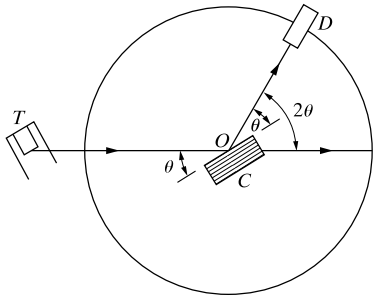


Figure 8 The x-ray spectrometer.

is parallel to its surface, as suggested by the drawing. In use, the crystal is positioned so that its diffracting planes make some particular angle θ with the incident beam, and D is set at the corresponding angle 2θ. The intensity of the diffracted beam is then measured and its wavelength calculated from Bragg's law, this procedure being repeated for various angles θ. W. H. Bragg designed and used the first x-ray spectrometer, and the Swedish physicist Siegbahn developed it into an instrument of very high precision.

X-ray spectroscopy is of concern only insofar as it concerns certain units of wavelength. Wavelength measurements made in the way just described are obviously relative, and their accuracy is no greater than the accuracy with which the plane spacing of the crystal is known.

Before considering how the first plane spacing was determined, first consider the subject of *x-ray density*. Normally the density of a solid is found by measuring the volume, usually of the order of a few cubic centimeters, and the weight of a particular specimen. But x-ray diffraction allows measurement of the lattice parameters of a crystal's unit cell, and therefore its volume, together with the number of atoms in the cell. Density determination can be based not on a few cubic centimeters but on the volume of a single unit cell, by defining the

$$\text{x–ray density} = \frac{\text{weight of atoms in unit cell}}{\text{volume of unit cell}}.$$

$$\rho = \frac{\sum A/N}{V}, \tag{13}$$

where ρ = density (g/cm^3), ΣA = sum of the atomic weights of all the atoms in the unit cell, N = Avogadro's number, and V = volume of unit cell (cm^3). Inserting the value of N produces

$$\rho = \frac{\sum A}{NV} = \frac{\sum A}{(6.02257 \times 10^{23})(V' \times 10^{-24})} = \frac{1.66042 \sum A}{V'}, \tag{14}$$

where ρ is in g/cm^3 and V' is the unit-cell volume in Å^3.

The macroscopic density of a particular specimen, determined from the weight and volume of that specimen, is usually less than, and cannot exceed, the x-ray density, because the macroscopic specimen will usually contain cracks and pores on the macroscopic scale and vacancies in the lattice on the atomic scale. The x-ray density is therefore a useful quantity to know. Comparing it to the macroscopic density of, for example, a pressed and sintered metal or ceramic compact, determines the percent porosity in the compact. X-ray densities are sometimes loosely called "theoretical densities"; they are not theoretical because they are determined experimentally.

To return to the problem of wavelength determination, it is an interesting and crucial fact that Bragg was able to solve the crystal structure of NaCl without knowing the wavelength of the x-rays being diffracted. All he knew—all he needed to know—was that there was one *single*, strong wavelength in the radiation from the x-ray tube, namely, the strong $K\alpha$ line of the tube target. Once the NaCl structure is known, it follows that there are four sodium and four chlorine atoms per unit cell, and that

$$\sum A = 4(\text{at. wt. Na}) + 4(\text{at. wt. Cl}).$$

If this value is inserted into Eq. (13) together with the macroscopic density ρ, the volume V' of the unit cell can be found. Because NaCl is cubic, the lattice parameter a is given simply by the cube root of V'. From this value of a and the cubic plane-spacing equation the spacing of any set of planes can be found.

In this way, Siegbahn obtained a value of 2.814 Å for the spacing of the (200) planes of rock salt (NaCl), which he could use as a basis for wavelength measurements [9]. This spacing was known to only four significant figures, because it was derived from a macroscopic density of that precision. However, Siegbahn was able to measure wavelengths in terms of this spacing much more accurately, namely, to six significant figures. Not wishing to throw away the high relative precision he could attain, he wisely decided to arbitrarily define a new unit in which relative wavelengths could be expressed. This was the X unit (XU), so called because its true value in absolute units (angstroms) was unknown. By defining the (200) spacing of rock salt to six significant figures as 2814.00 XU, the new unit was made as nearly as possible equal to 0.001 Å.

Once a particular wavelength was determined in terms of this spacing, the spacing of a given set of planes in any other crystal could be measured. Siegbahn thus measured the (211) spacing of calcite ($CaCO_3$), which he found more suitable as a standard crystal, and thereafter based all his wavelength measurements on this spacing. Its value is 3029.45 XU. Later on, the kilo X unit (kX) was introduced, a thousand times as large as the X unit and nearly equal to an angstrom. The kX unit is therefore *defined* by the relation

$$1\ \text{kX} = \frac{(211)\ \text{plane spacing of calcite}}{3.02945}. \tag{15}$$

On this basis, Siegbahn and coworkers made very accurate measurements of wavelength in relative (kX) units and these measurements form the basis of most published wavelength tables.

It was found later that x-rays could be diffracted by a ruled grating such as is used in the spectroscopy of visible light, provided that the angle of incidence (the angle between the incident beam and the plane of the grating) is kept below the critical angle for total reflection. Gratings thus offer a means of making absolute wavelength measurements, independent of any knowledge of crystal structure. By

a comparison of values so obtained with those found by Siegbahn from crystal diffraction, it was possible to calculate the following relation between the relative and absolute units:

$$1\ \text{kX} = 1.00202\text{Å}.$$

This conversion factor was adopted in 1946 by international agreement. Later work improved the accuracy of this factor, and the relation is now believed to be

$$1\ \text{kX} = 1.002056\text{Å}^*. \tag{16}$$

Note that this relation is stated in terms of still another unit, the Å^* unit, which was introduced because of the still remaining uncertainty in the conversion factor. The difference between Å and Å^* is only some five parts per million, and the distinction between the two units is negligible except in work of the very highest accuracy.

The present situation is not entirely clear, but the wavelength tables published by the International Union of Crystallography [Vol. C, G.1] are the best available value.

The distinction between kX and Å is unimportant if no more than about three significant figures are involved, because the kX unit is only about 0.2 percent larger than the angstrom. In precise work, on the other hand, units must be correctly stated, and on this point there has been considerable confusion in the past. Some wavelength values published prior to about 1946 are stated to be in angstrom units but are actually in kX units. Some crystallographers have used such a value as the basis for a precise measurement of the lattice parameter of a crystal, and the result has been stated, again incorrectly, in angstrom units. Many published parameters are therefore in error, and it is unfortunately not always easy to determine which ones are and which ones are not. The only safe rule to follow, in stating a precise parameter, is to give the wavelength of the radiation used in its determination. Similarly, any published table of wavelengths can be tested for the correctness of its units by noting the wavelength given for a particular characteristic line, Cu $K\alpha_1$ for example. The wavelength of this line is 1.540562 Å^* (1974 value, 1.002056 as conversion factor), 1.54051 Å (1946 value, 1.00202 factor), or 1.53740 kX.

8 DIFFRACTION METHODS

Diffraction can occur whenever Bragg's law, $\lambda = 2d \sin\theta$, is satisfied. This equation puts very stringent conditions on λ and θ for any given crystal. With monochromatic radiation, an arbitrary setting of a single crystal in a beam of x-rays will not in general produce *any* diffracted beams. Some way of satisfying Bragg's law must be devised, and this can be done by continuously varying either λ or θ during the experiment. The ways in which these quantities are varied distinguish three main diffraction methods:

Method	λ	θ
Laue	Variable	Fixed
Rotating-crystal	Fixed	Variable (in part)
Powder	Fixed	Variable

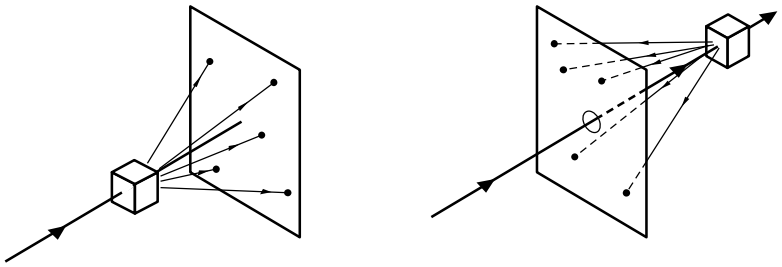
Laue Method

The Laue method was the first diffraction method ever used, and it reproduces von Laue's original experiment. In this method, a beam of white radiation, the continuous spectrum from an x-ray tube, falls on a fixed single crystal. The Bragg angle θ is therefore fixed for every set of planes in the crystal, and each set selects and diffracts that particular wavelength which satisfies Bragg's law for the particular values of d and θ involved. Each diffracted beam thus has a different wavelength.

There are two variations of the Laue method, depending on the relative positions of source, crystal, and film (Fig. 9). In each, the film is flat and placed perpendicular to the incident beam. The film in the *transmission Laue method* (the original Laue method) is placed behind the crystal so as to record the beams diffracted in the forward direction. This method is so called because the diffracted beams are partially transmitted through the crystal. In the *back-reflection Laue method* the film is placed between the crystal and the x-ray source, the incident beam passing through a hole in the film, and the beams diffracted in a backward direction are recorded.

In either method, the diffracted beams form an array of spots on the film as shown in Fig. 10. This array of spots is commonly called a *pattern*, but the term is not used in any strict sense and does not imply any periodic arrangement of the spots. On the contrary, the spots are seen to lie on certain curves, as shown by the lines drawn on the photographs. These curves are generally ellipses or hyperbolas for transmission patterns [Fig. 10(a)] and hyperbolas for back-reflection patterns [Fig. 10(b)].

The spots lying on any one curve are reflections from planes belonging to one



(a) (b)

Figure 9 (a) Transmission and (b) back-reflection Laue methods.

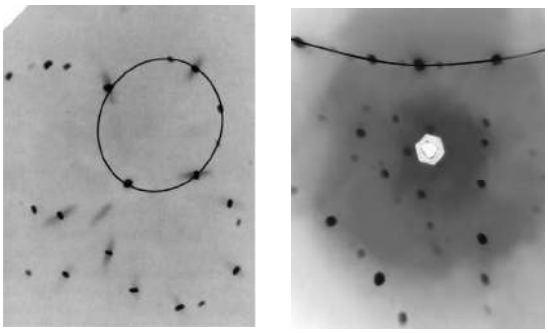


Figure 10 (a) Transmission and (b) back-reflection Laue patterns of an aluminum crystal (cubic). Tungsten radiation, 30 kV, 19 mA.

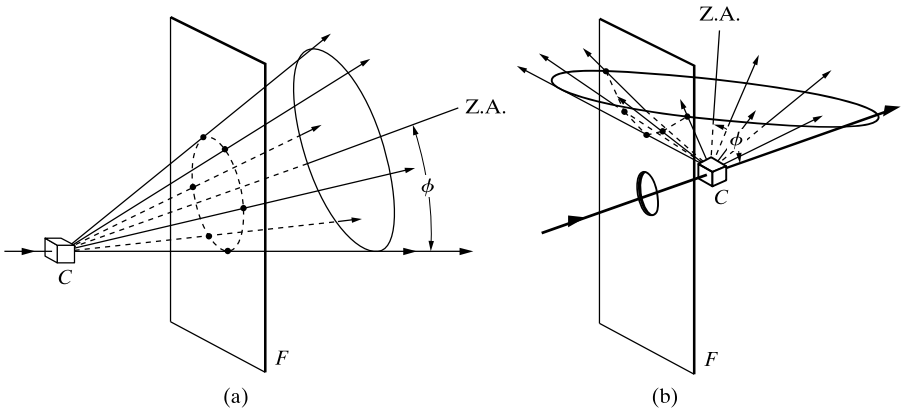


Figure 11 Location of Laue spots (a) on ellipses in transmission method and (b) on hyperbolas in back-reflection method. (*C* = crystal, *F* = film, Z.A. = zone axis.)

zone. This is due to the fact that the Laue reflections from planes of a zone all lie on the surface of an imaginary cone whose axis is the zone axis. As shown in Fig. 11(a), one side of the cone is tangent to the transmitted beam, and the angle of inclination ϕ of the zone axis (Z.A.) to the transmitted beam is equal to the semi-apex angle of the cone. A film placed as shown intersects the cone in an imaginary ellipse passing through the center of the film, the diffraction spots from planes of a zone being arranged on this ellipse. When the angle ϕ exceeds 45°, a film placed between the crystal and the x-ray source to record the back-reflection pattern will intersect the cone in a hyperbola, as shown in Fig. 11(b).

The fact that the Laue reflections from planes of a zone lie on the surface of a cone can be demonstrated nicely with the stereographic projection. In Fig. 12, the crystal is at the center of the reference sphere, the incident beam *I* enters at the left, and the transmitted beam *T* leaves at the right. The point representing the zone axis

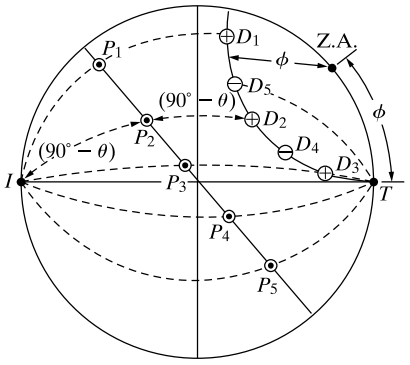


Figure 12 Stereographic projection of transmission Laue method.

lies on the circumference of the basic circle and the poles of five planes belonging to this zone, P_1 to P_5, lie on the great circle shown. The direction of the beam diffracted by any one of these planes, for example the plane P_2, can be found as follows. I, P_2, D_2 (the diffraction direction required), and T are all co-planar. Therefore D_2 lies on the great circle through I, P_2, and T. The angle between I and P_2 is $(90^\circ - \theta)$, and D_2 must lie at an equal angular distance on the other side of P_2, as shown. The diffracted beams so found, D_1 to D_5, are seen to lie on a small circle, the intersection with the reference sphere of a cone whose axis is the zone axis.

The positions of the spots on the film, for both the transmission and the back-reflection method, depend on the orientation of the crystal relative to the incident beam, and the spots themselves become distorted and smeared if the crystal has been bent or twisted in any way. These facts account for the two main uses of the Laue methods: the determination of crystal orientation and the assessment of crystal quality.

The Ewald sphere treatment of diffraction of a single wavelength λ from a crystal can be readily extended to the Laue method where multiple λ are incident. The range of wavelengths used is represented by a series of parallel incident beams, each with a different length proportional to $1/\lambda_i$. Note that each of these vectors terminates at the origin of the reciprocal lattice, and each has a different origin (Fig. 13). Thus, each incident beam S_o/λ_i has a corresponding Ewald sphere touching the origin of the reciprocal lattice and having radius $1/\lambda_i$. All of the different S_o/λ_i pass through the origin of the reciprocal lattice, and the corresponding Ewald spheres have centers lying on the line **OACDB** of Fig. 13, i.e., the incident beam direction. The range of wavelengths present in the incident beam is of course not infinite. It has a sharp lower limit at λ_{SWL}, the short-wavelength limit of the continuous spectrum; the upper limit is less definite and depends on experimental factors such as whether the transmission or back-reflection geometry is being used. In the example of the Ewald sphere construction shown in Fig. 13, the upper wavelength limit is taken as the wavelength of the K absorption edge of the silver in the emulsion (0.48 Å), because the effective photographic intensity of the continuous spectrum drops abruptly at that wavelength. This choice is most appropriate for trans-

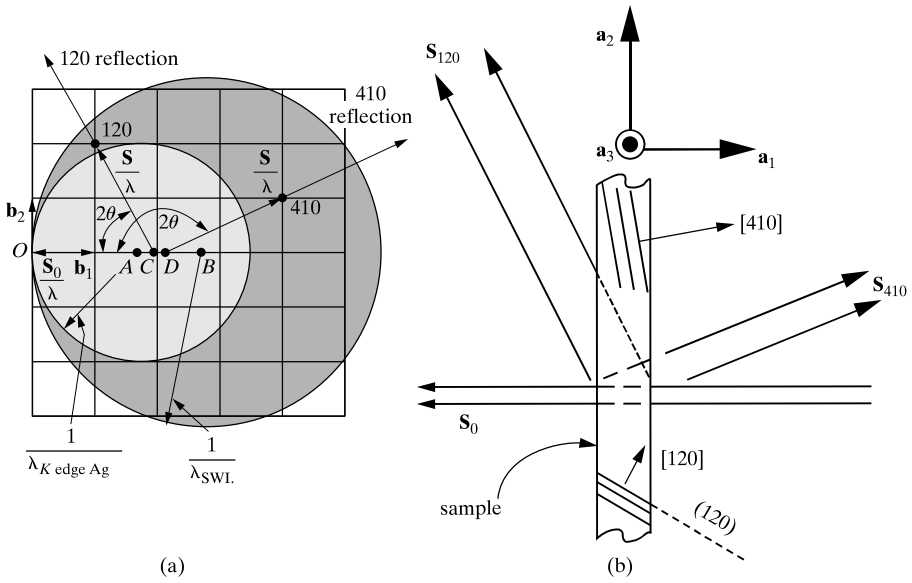


Figure 13 Reciprocal lattice (a) and corresponding schematic of the crystal in direct space (b) for the Laue method. $(\mathbf{S} - \mathbf{S}_0)/\lambda = \mathrm{H}$.

mission Laue patterns of crystals which are quite absorbing since the value of the linear attenuation coefficient (of an element in a sample) rises rapidly with increasing wavelength. For back-reflection Laue patterns considerable darkening of the film wll occur for wavelengths above the silver edge and below the bromine K-edge as well as for somewhat longer wavelengths.

To these two extreme wavelengths correspond two extreme Ewald spheres, as shown in Fig. 13, which is a section through these spheres and the $l = 0$ layer of the reciprocal lattice. The incident beam is along the $\mathbf{b}_1$ vector, i.e., perpendicular to the (h00) planes of the crystal. The larger sphere shown is centered at B and has a radius equal to the reciprocal of λ_{SWL}, while the smaller sphere is centered at A and has a radius equal to the reciprocal of the wavelength of the silver K absorption edge. A whole series of spheres lie between these two, and any reciprocal-lattice point lying in the shaded region of the diagram is on the surface of one of these spheres and corresponds to a set of crystal planes oriented to diffract one of the incident wavelengths. In the forward direction, for example, a 120 reflection will be produced. To find its direction, locate a point C on AB which is equidistant from the origin O and the reciprocal-lattice point 120; C is therefore the center of the Ewald sphere passing through the point 120. Joining C to 120 gives the diffracted-beam vector S/λ for this reflection. The direction of the 410 reflection, one of the many backward-diffracted beams, is found in similar fashion; here the reciprocal-lattice point in question is situated on a Ewald sphere centered at D.

Rotating-Crystal Method

In the rotating-crystal method a single crystal is mounted with one of its axes, or some important crystallographic direction, normal to a monochromatic x-ray beam. A cylindrical film is placed around it and the crystal is rotated about the chosen direction, the axis of the film coinciding with the axis of rotation of the crystal (Fig. 14). As the crystal rotates, a particular set of lattice planes will, for an instant, make the correct Bragg angle for diffraction of the monochromatic incident beam, and at that instant a diffracted beam will be formed. The diffracted beams are again located on imaginary cones but now the cone axes coincide with the rotation axis. The result is that the spots on the film, when the film is laid flat, lie on imaginary horizontal "layer" lines, as shown in Fig. 15. Since the crystal is rotated about only one axis, the Bragg angle does not take on all possible values between 0° and 90° for every set of planes. Not every set, therefore, is able to produce a diffracted beam; sets perpendicular or almost perpendicular to the rotation axis are examples.

The Ewald sphere construction for monochromatic radiation can be used to illustrate why beams diffracted from a single crystal rotated about one of its axes lie on the surface of cones coaxial with the rotation axis. This interpretation of the patterns of diffraction spots was emphasized by Bernal [10]. Suppose a simple cubic crystal is rotated about the axis [001]. This is equivalent to rotation of the reciprocal lattice about the $\mathbf{b}_3$ axis. Figure 16 shows a portion of the reciprocal lattice oriented in this manner, together with the adjacent Ewald sphere.

All crystal planes having indices $(hk1)$ are represented by points lying on a plane (called the "$l = 1$ layer") in the reciprocal lattice, normal to $\mathbf{b}_3$. When the reciprocal lattice rotates, this plane cuts the Ewald sphere in the small circle shown, and any

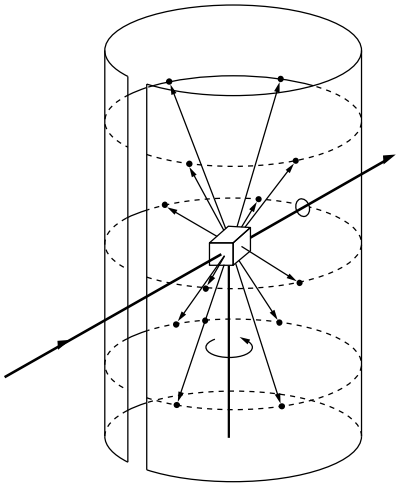


Figure 14 Rotating-crystal method.

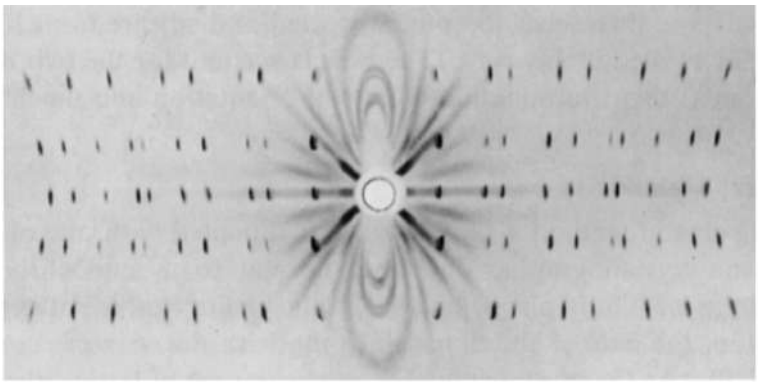


Figure 15 Rotating-crystal pattern of a quartz crystal (hexagonal) rotated about its c axis. Filtered copper radiation. (The streaks are due to the white radiation not removed by the filter.) (Courtesy of B. E. Warren.)

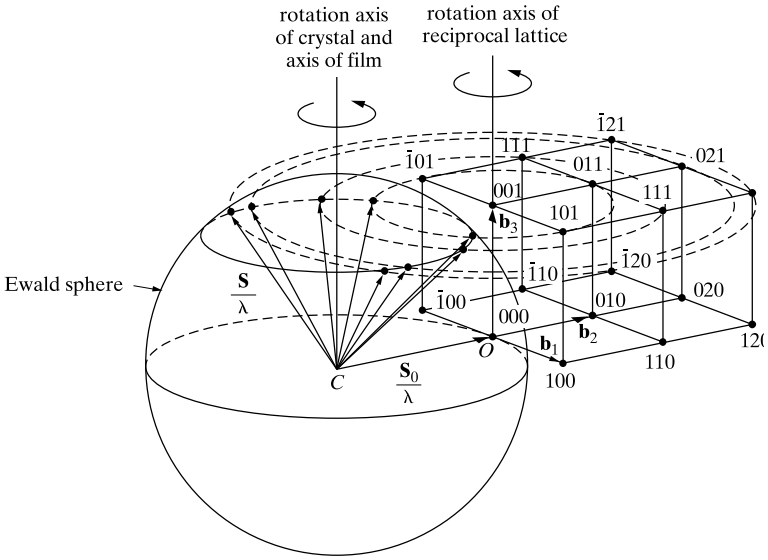


Figure 16 Reciprocal-lattice treatment of rotating-crystal method.

points on the $l = 1$ layer which touch the sphere surface must touch it on this circle. Therefore all diffracted-beam vectors S/λ must end on this circle, which is equivalent to saying that the diffracted beams must lie on the surface of a cone. In this par-

ticular case, all the *hk*1 points shown intersect the surface of the sphere sometime during their rotation about the $\mathbf{b}_3$ axis, producing the diffracted beams shown in Fig. 16. In addition many *hk0* and *hk*1 reflections would be produced, but these have been omitted from the drawing for the sake of clarity.

The chief use of the rotating-crystal method and its variations were in the determination of unknown crystal structures, but the complete determination of complex crystal structures is a subject beyond the scope of this book and outside the province of the average materials scientist/engineer who uses x-ray diffraction as a laboratory tool. Analyzing patterns consisting of layer lines of diffraction spots remains important however, for polymers and is beyond the scope of this chapter.

Powder Method

In the powder method, the crystal to be examined is reduced to a very fine powder or already is in the form of loose or consolidated microscopic grains. The sample in a suitable holder is placed in a beam of monochromatic x-rays. Each particle of the powder is a tiny crystal, or assemblage of smaller crystals, oriented at random with respect to the incident beam. Just by chance, some of the crystals will be correctly oriented so that their (100) planes, for example, can diffract the incident beam. Other crystals will be correctly oriented for 110 reflections, and so on. The result is that every set of lattice planes will be capable of diffraction. The mass of powder is equivalent, in fact, to a single crystal rotated, not about one axis, but about all possible axes.

Consider one particular *hkl* reflection, and remember that $\mathbf{S}, \mathbf{S}_0$ and $\mathbf{N}_{hkl}$, the normal to the diffraction planes (*hkl*), must be coplanar. One or more little crystals will, by chance, be so oriented that their (*hkl*) planes make the correct Bragg angle for diffraction; Fig. 17(a) shows one plane in this set and the diffracted beam formed. If this plane is now rotated about the incident beam in such a way that θ is kept constant, then the diffracted beam will travel over the surface of a cone as shown in Fig. 17 (b), the axis of the cone coinciding with the transmitted beam.

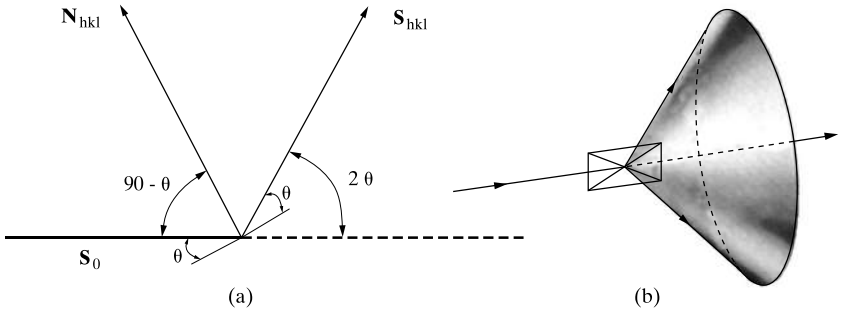


Figure 17 Formation of a diffracted cone of radiation in the powder method.

Equivalently, one can imagine rotating N_{hkl} about $\mathbf{S}_0$ while keeping the angle between them equal to $90° - \theta$ degrees.

This rotation does not actually occur, but the presence of a large number of crystal particles having all possible orientations is equivalent to this rotation, since among these particles there will be a certain fraction whose (*hkl*) planes make the correct Bragg angle with the incident beam and which at the same time lie in all possible rotational positions about the axis of the incident beam. The *hkl* reflection from a stationary mass of powder thus has the form of a conical sheet of diffracted radiation, and a separate cone is formed for each set of differently spaced lattice planes.

Figure 18 shows three such cones and also illustrates a common powder-diffraction method. In this, the Hull/Debye–Scherrer method [11, 12], a narrow strip of film is curved into a short cylinder with the specimen placed on its axis and the incident beam directed at right angles to this axis. [8] The cones of diffracted radiation intersect the cylindrical strip of film in lines, and when the strip is unrolled and laid flat, the resulting pattern appears as in Fig. 18(b). Actual patterns, produced by various metal powders, are shown in Fig. 19. Each diffraction line is made up of a large number of small spots, each from a separate crystal particle, the spots lying so close together that they appear as a continuous line. The lines are generally curved, unless they occur exactly at $2\theta = 90°$ when they will be straight. From the measured position of a given diffraction line on the film, θ can be determined, and from θ, knowing λ, the spacing d of the diffracting lattice planes which produced the line.

Conversely, if the shape and size of the unit cell of the crystal are known, the position of all possible diffraction lines on the film can be predicted. The line of lowest 2θ value is produced by diffraction from planes of the greatest spacing. In the cubic system, for example, d is a maximum when $(h^2 + k^2 + l^2)$ is a minimum, and the minimum value of this term is l, corresponding to (*hkl*) equal to (100). The 100 reflection is accordingly the one of lowest 2θ value. The next possible reflection will have indices *hkl* corresponding to the next higher value of $(h^2 + k^2 + l^2)$, namely 2, in which case (*hkl*) equals (110), and so on.

The reciprocal lattice of a randomly oriented powder sample consists of a series of reciprocal lattice (rel) shells centered on the origin of the reciprocal lattice. Remembering that all orientations are equally likely for a random powder sample, constructing the reciprocal lattice representing the powder is straight-forward: first draw the reciprocal lattice for a single grain and second rotate the reciprocal lattice points through all possible orientations. Each reciprocal lattice point *hkl* for the crystal becomes, therefore, a sphere of radius $1/d_{hkl}$, centered on the reciprocal lattice origin (Fig. 20a). For an incident beam $\mathbf{S}_0$ and Bragg angles θ_{hkl}, a number of $\mathbf{S}_{hkl}$

[8] Most authors term this technique the Debye–Scherrer method, but it seems reasonable to acknowledge the independent and more-or-less simultaneous development in the US and Germany during the First World War.

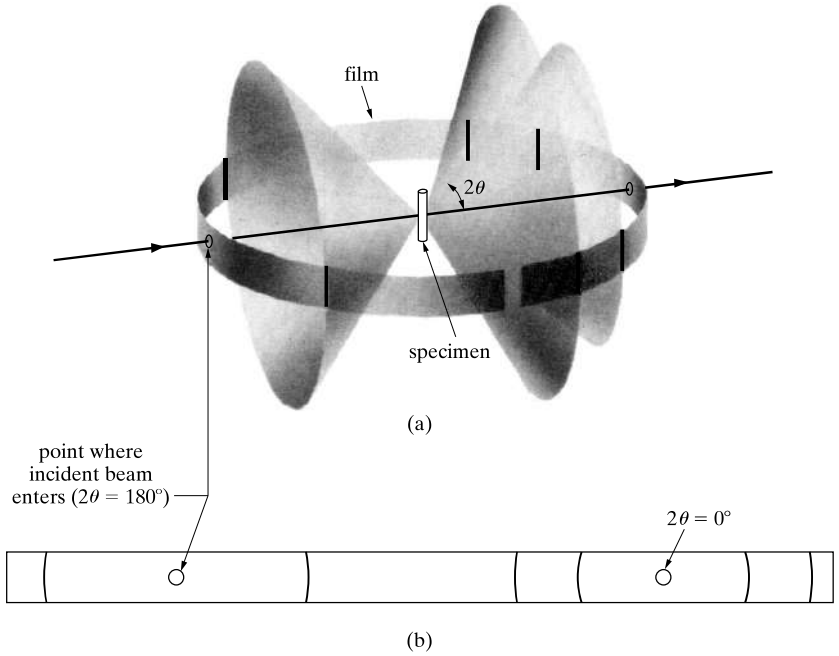


Figure 18 Hull/Debye–Scherrer powder method: (a) relation of film to specimen and incident beam; (b) appearance of film when laid flat.

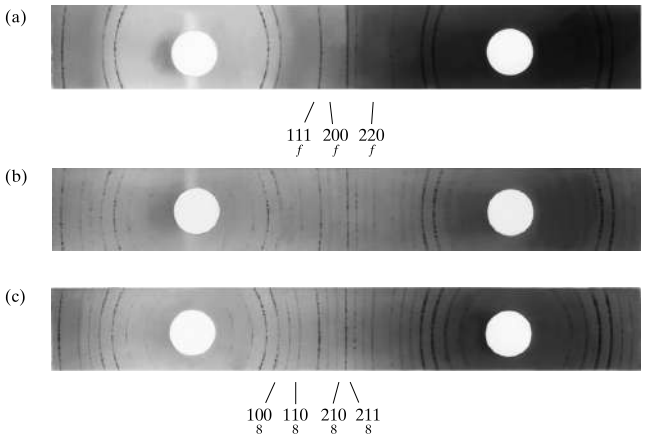


Figure 19 Hull/Debye–Scherrer powder patterns of copper (FCC), tungsten (BCC), and zinc (HCP). Filtered copper radiation, camera diameter = 5.73 cm.

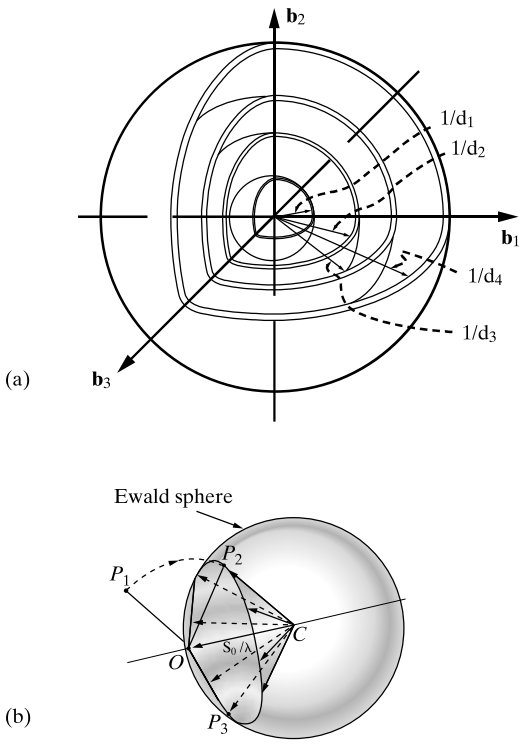


Figure 20 (a) Reciprocal lattice shells with radii $1/d_1$, $1/d_2$, $1/d_3$ and $1/d_4$, and (b) diffraction cones from the intersection of a reciprocal lattice shell and the Ewald sphere. When P_1 is rotated about the reciprocal lattice origin, it intersects the Ewald sphere at P_2, P_3 and other points of a circle.

simultaneously satisfy Bragg's law. The loci of $\mathbf{S}_{hkl}$ are determined by the intersection of the rel shells and the Ewald sphere and consist of a series of cones centered on $\mathbf{S}_0$ (diffraction in the forward direction) or on $-\mathbf{S}_0$ (diffraction in back-reflection). The formation of one such cone is illustrated in Fig. 20b, but for clarity the Ewald sphere is pictured and the reciprocal lattice shells are omitted. Instead, reciprocal lattice point P on one shell is rotated through all possible orientations. The resulting intersection of the shell and the Ewald sphere is a circle, and the locus of $\mathbf{S}_{hkl}$ is a cone.

The x-ray spectrometer can be used as a tool in diffraction analysis. This instrument is known as a *diffractometer* when it is used with x-rays of *known* wave-length to determine the *unknown* spacing of crystal planes [13], and as a spectrometer in the reverse case, when crystal planes of known spacing are used to determine

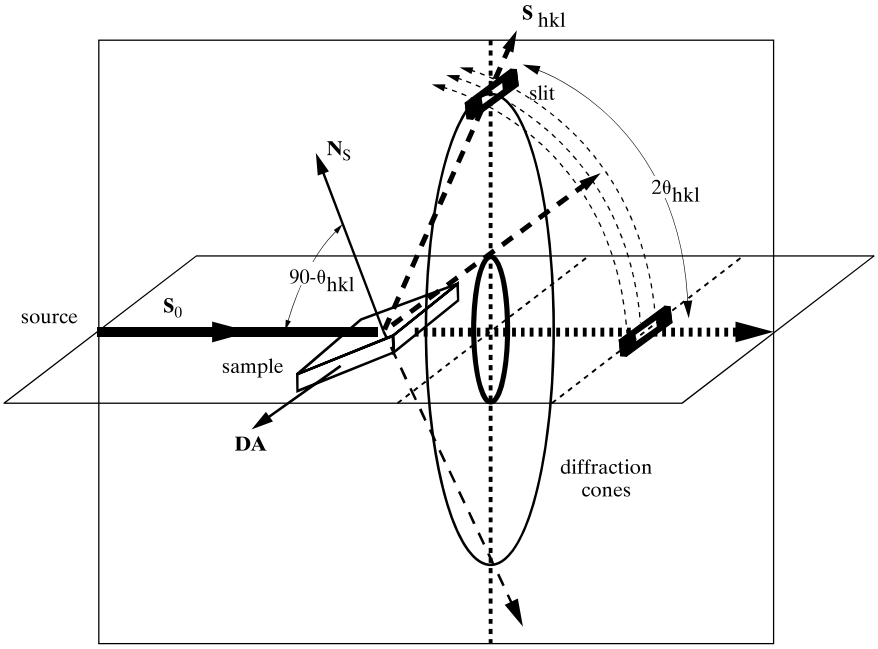


Figure 21 Illustration of the role of the slit on the detector in measuring diffraction peaks in powder diffractometry. Two diffraction cones are shown, $\mathbf{N_S}$ is the normal to the sample, **DA** is the diffractometer rotation axis; and $\mathbf{S}_0$, $\mathbf{N_S}$ and the portions of $\mathbf{S}_1$ and $\mathbf{S}_2$ (portions of the cones intersecting the slit) are coplanar.

unknown wavelengths. The diffractometer is always used with monochromatic radiation and measurements may be made on either single crystals or polycrystal line specimens (early developments are outline in [G.17 and G.18]), the detector intercepts and measures only a short arc of any one cone of diffracted rays (Fig. 21). Note that the diffractometer's receiving slit is essential to the observation of diffraction peaks of randomly-oriented, fine-grained powders. The diffraction cones are always present; in fact, cones for all possible *hkl* are present simultaneously. The receiving slit is necessary to eliminate all diffracted radiation except that passing through this very narrow angular window.

Different powder diffraction techniques sample different portions of reciprocal space, and a complete understanding of diffraction phenomena from a reciprocal space perspective requires rigorous definition of the reciprocal space sampling region for each technique. Developing such an understanding is beyond the scope of this book, and the reader is referred to more comprehensive treatments of reciprocal space [5].

The Hull/Debye–Scherrer and other camera methods and the diffractometer are very widely used. Powder diffraction is, of course, the only method that can be

employed when a single-crystal specimen is not available, and this is the case more often than not in materials work. The method is especially suited for determining lattice parameters with high precision and for the identification of phases, whether they occur alone or in mixtures such as polyphase alloys, corrosion products, refractories, and rocks.

9 EXPERIMENTAL VISUALIZATION OF THE RECIPROCAL LATTICE

The preceding section discussed how the rotating crystal method allowed imaging of the distribution of reciprocal lattice points in space. Transmission electron microscopy (TEM) also images the reciprocal lattice directly: planes through the reciprocal lattice can be seen in certain TEM operating modes. In TEM there are a series of three or more lenses following the sample and providing the high magnifications which make the TEM so useful for materials characterization. The wavelike properties of electrons allow them to diffract from crystalline samples. Typically in TEM, electrons are accelerated to 100 keV or higher and have wavelengths of 0.037 Å or lower. This acceleration allows the electrons to be transmitted through samples whose thicknesses are on the order of 1000 Å. Because electrons carry a charge, magnetic lenses are effective at focusing electrons (unlike the case of x-rays where lenses can deflect the photons only a minescule fraction of a degree.) It is important to note that most materials' TEM imaging of materials relies on diffracted electrons to provide image contrast.

The very small wavelength of the electrons means that the radius of the corresponding Ewald sphere is very large compared to the spacing between reciprocal lattice points or compared to the Ewald sphere diameter for x-rays. For 0.037 Å radiation, the Ewald sphere radius is 25 $Å^{-1}$ compared to ~1 $Å^{-1}$ for x-rays and to ~0.5 $Å^{-1}$ for the reciprocal lattice spacing. This means that the curvature of the Ewald sphere is gradual compared to the reciprocal lattice spacings, and that, in the vicinity of the origin of the reciprocal lattice, the Ewald sphere is essentially a plane cutting through the reciprocal lattice (Fig. 22). As will be seen in Ch. 4, the sample's thinness produces reciprocal lattice points which are elongated along the thin axis of the sample, i.e., rel rods or reciprocal lattice rods, and the rods intersect the Ewald sphere over quite a large range of 1/d. This section of the reciprocal lattice

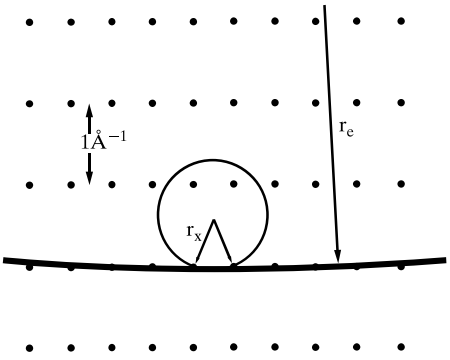


Figure 22 Reciprocal lattice of the orthorhombic crystal shown in Fig. 6 with the Ewald spheres and radii r_x for Cu $K\alpha$ x-rays and r_e for 100 keV electrons.

imaged by the TEM is termed a diffraction pattern and is normally identified by the direction of incidence of the electrons, i.e., by the normal to the reciprocal lattice plane.

The TEM ray diagram pictured in Fig. 23 shows how an image of the sample or an image of the sample's diffraction pattern is obtained. The incident electrons are indicated by the arrows at the top of the figure, and one diffracted beam **G** and the transmitted beam **O** originating from each of three points (A, B and C) in the sample illustrate the electron-sample interactions of interest here. The diffracted and transmitted beams pass through the objective lens whose optic axis is **BB´**. Parallel rays are brought to a focus in the diffraction plane, and rays diverging from a point are recombined in the image plane. In other words, the three rays **G** from A, B and C are combined at G in the diffraction plane, and the rays **G** and **O** from A recombine at A´ in the image plane. If the other lenses of the TEM are focussed on the diffraction plane, the essentially planar section of the reciprocal lattice is imaged. If focussing is on the image plane, an image of the sample results. In other words, parallel directions are mapped onto a single point in the diffraction plane in just as all (*hkl*) in direct space were mapped onto point *hkl* in reciprocal space.

Figure 24 shows a diffraction pattern recorded from a grain of NiAl with the electron beam parallel to [100]. The four-fold symmetry expected along <100> in the CsCl structure is clearly seen. Multiple orders of each diffraction vector are seen simultaneously, an apparent contradiction of Bragg's law: for a single wavelength Bragg's law predicts that first and second order diffraction (*hkl* and 2*h* 2*k* 2*l*) occur at angles θ_{hkl} and θ_{2h2k2l} given, for cubic axial systems, by

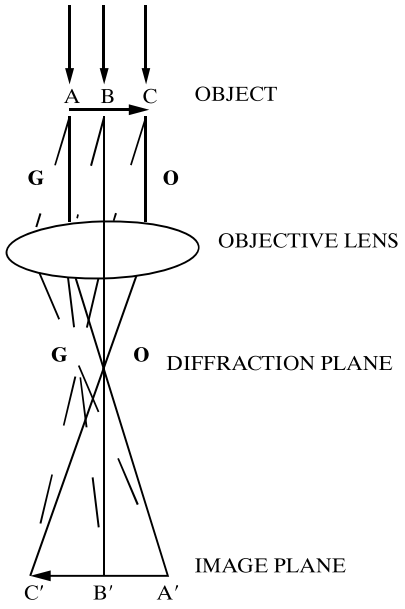


Figure 23 TEM ray diagram showing the diffraction plane and image plane.

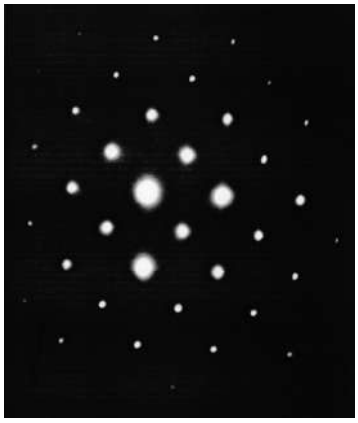


Figure 24 001 diffraction pattern from a grain of NiAl.

$$\sqrt{2}\sin\theta_{hkl} = \sin\theta_{2h2k2l}.$$

The question is how first and second order diffraction can occur simultaneously for the same angle of incidence of $\mathbf{S}_0$ if small rotations from the Bragg angle destroy constructive interference. Stated in other terms, the derivation of Bragg's law implicitly assumed that the diffraction peaks are delta functions, i.e., that the crystal has an infinitely narrow range of reflection.

The resolution to this apparent contradiction lies in the fact that *Bragg's law describes diffraction incompletely*. Very small crystal or grain dimensions have very wide diffraction ranges as a direct consequence of their small size. In other words, significant diffracted intensity occurs at angles off the exact Bragg condition, but development of an understanding of the factors governing diffracted intensity must precede discussion of how far a crystal must rotate before diffracted intensity drops to zero.

10 DIFFRACTION UNDER NONIDEAL CONDITIONS

In Sec 9, the discussion of diffraction patterns illustrated one consequence of deviation for "ideality". Before going any further, it is important to consider other aspects of the derivation of Bragg's law given in Sec. 2 in order to understand precisely under what conditions it is strictly valid. In the derivation certain ideal conditions were assumed, namely a perfect crystal and an incident beam composed of perfectly parallel and strictly monochromatic radiation. These conditions never actually exist. For example, the incident x-ray beam in most powder diffractometers is divergent and the characteristic lines from x-ray tubes have finite spectral widths. Also implicit is that once x-ray photons are diffracted they will not be re-directed; this assumption, the basis of kinematical diffraction theory, holds except for diffraction from thick, highly perfect crystals.

Imperfections in the crystal(s) making up a sample can broaden the diffraction peaks. Only the infinite crystal is really perfect and small size alone, of an otherwise

perfect crystal, can be considered a crystal imperfection, and can lead to peak broadening. The presence of large numbers of dislocations (i.e., strain) in the grains of a sample can produce significant peak broadening. The inference of sample strain or crystallite size from peak widths (or shapes) is an important part of diffraction analysis of materials.

PROBLEMS

1 A transmission Laue pattern is made of a cubic crystal having a lattice parameter of 4.00 Å. The x-ray beam is horizontal. The $[0\bar{1}0]$ axis of the crystal points along the beam towards the x-ray tube, the $[\bar{1}00]$ axis points vertically upward, and the [001] axis is horizontal and parallel to the photographic film. The film is 5.00 cm from the crystal.

a) What is the wavelength of the radiation diffracted from the $(\bar{3}\bar{1}0)$ planes?

b) Where will the $\bar{3}\bar{1}0$ reflection strike the film?

*__2__ A transmission Laue pattern is made of a cubic crystal in the orientation of Prob. 1. By means of a stereographic projection similar to Fig. 12, show that the beams diffracted by the planes $(\bar{2}\bar{1}0)$, $(\bar{2}\bar{1}3)$, and (211), all of which belong to the zone $[\bar{1}20]$, lie on the surface of a cone whose axis is the zone axis. What is the angle ϕ between the zone axis and the transmitted beam?

3 Determine, and list in order of increasing angle, the values of 2θ and (hkl) for the first three lines (those of lowest 2θ values) on the powder patterns of substances with the following structures, the incident radiation being Cu $K\alpha$:

a) simple cubic (a = 3.00 Å),

b) simple tetragonal (a = 2.00 Å, c = 3.00 Å),

c) simple tetragonal (a = 3.00 Å, c = 2.00 Å),

d) simple rhombohedral (a = 3.00 Å, $\alpha = 80°$).

4 Plot the reciprocal lattice for a polycrystalline sample of a material with a simple tetragonal structure and lattice parameters a = 4.0 Å and c = 5.0 Å. (Use a two-dimensional section through the three-dimensional space).

5 Sketch the Ewald sphere construction for 200 diffraction with Mo $K\alpha$ radiation and a polycrystalline specimen of a simple cubic substance with a = 3.30 Å. Graphically determine the angular rotation required to orient the sample for 300 diffraction if a $\theta - 2\theta$ diffractometer is being used.

6 Diffractometers typically can scan up to, but not beyond, 165° 2θ. For the sample in Problem 4, what are the indices (i.e., hkl) of the highest angle reflection if (a) Ag $K\alpha$ radiation is used, (b) Cu $K\alpha$ radiation is used and c) Cr $K\alpha$ radiation is used?

REFERENCES

The following books are listed more or less in the order they are encountered in the text

G.1 *International Tables for Crystallography*, Ed. A.J.C Wilson, Vol. A-C (Dordrecht Kluwer Academic Pub. for International Union of Crystallography, 1995). The reference ''book" for crystallography and diffraction.

G.11 P. P. Ewald, ed. *Fifty Years of X-Ray Diffraction* (Utrecht: International Union of Crystallography, 1962.) See pp. 31-56 and 293-294 for accounts of the von laue experiment. The early work of the Braggs is described on pp. 57-73 120-123, and 532-533. This interesting volume also contains the personal reminiscences of many eminent x-ray crystallographers.

G.13 André Guinier. *X-Ray Crystallographic Technology* (London: Hilger and Watts, 1952). Excellent treatment of the theory and practice of x-ray diffraction. The title is not fair to the book, which includes a considerable body of theory and detailed experimental technique. The theory and applications of the reciprocal lattice are very well described. Includes treatments of focusing monochromators, small-angle scattering, and diffraction by amorphous substances.

G.17 Harold P. Klug and Leroy E. Alexander. *X-Ray Diffraction Procedures*, 2nd ed. (New York: Wiley, 1974). Contains a great deal of useful detail on the theory and operation of powder cameras and diffractometers. Covers the following topics in depth: chemical analysis by diffraction, parameter measurement, line-broadening analysis, texture determination, stress measurement, and studies of amorphous materials. Single-crystal methods are not included.

G.18 W. Parrish, ed. *Advances in X-ray diffractometry and X-ray Spectrography* (Eindhoven: Centrex Pub. Co., 1962).

ANSWERS TO SELECTED PROBLEMS

2. 26.6°