6
Determination of Crystal Structures by X-ray Diffraction

Formulation of Bragg and von Laue

The Laue Condition and Ewald's Construction

Experimental Methods: Laue, Rotating Crystal, Powder

Geometrical Structure Factor

Atomic Form Factor

Typical interatomic distances in a solid are on the order of an angstrom (10^{-8} cm). An electromagnetic probe of the microscopic structure of a solid must therefore have a wavelength at least this short, corresponding to an energy of order

$$\hbar\omega = \frac{hc}{\lambda} = \frac{hc}{10^{-8} \text{ cm}} \approx 12.3 \times 10^3 \text{ eV}. \tag{6.1}$$

Energies like this, on the order of several thousands of electron volts (kilovolts or keV), are characteristic X-ray energies.

In this chapter we shall describe how the distribution of X rays scattered by a rigid,[1] periodic[2] array of ions reveals the locations of the ions within that 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 viewpoints are still widely used. The von Laue approach, which exploits the reciprocal lattice, is closer to the spirit of modern solid state physics, but the Bragg approach is still in wide use by X-ray crystallographers. Both are described below, together with a proof of their equivalence.

BRAGG FORMULATION OF X-RAY DIFFRACTION BY A CRYSTAL

In 1913 W. H. and W. L. Bragg found that substances whose macroscopic forms were crystalline gave remarkably characteristic patterns of reflected X-radiation, quite unlike those produced by liquids. In crystalline materials, for certain sharply defined wavelengths and incident directions, intense peaks of scattered radiation (now known as Bragg peaks) were observed.

W. L. Bragg accounted for this by regarding a crystal as made out of parallel planes of ions, spaced a distance d apart (i.e., the lattice planes described in Chapter 5). The conditions for a sharp peak in the intensity of the scattered radiation were: (1) that the X rays should be specularly reflected[3] by the ions in any one plane and (2) that the reflected rays from successive planes should interfere constructively. Rays specularly reflected from adjoining planes are shown in Figure 6.1. The path difference between the two rays is just $2d \sin \theta$, where θ is the angle of incidence.[4] For the rays to interfere constructively, this path difference must be an integral number of wavelengths, leading to the celebrated Bragg condition:

$$n\lambda = 2d \sin \theta. \tag{6.2}$$

The integer n is known as the order of the corresponding reflection. For a beam of X rays containing a range of different wavelengths ("white radiation") many different reflections are observed. Not only can one have higher-order reflections from a given set of lattice planes, but in addition one must recognize that there are

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[1]   Actually the ions vibrate about their ideal equilibrium sites (Chapters 21–26). This does not affect the conclusions reached in this chapter (though in the early days of X-ray diffraction it was not clear why such vibrations did not obliterate the pattern characteristic of a periodic structure). It turns out that the vibrations have two main consequences (see Appendix N): (a) the intensity in the characteristic peaks that reveal the crystal structure is diminished, but not eliminated; and (b) a much weaker continuous background of radiation (the "diffuse background") is produced.

[2]   Amorphous solids and liquids have about the same density as crystalline solids, and are therefore also susceptible to probing with X rays. However, the discrete, sharp peaks of scattered radiation characteristic of crystals are not found.

[3]   In specular reflection the angle of incidence equals the angle of reflection.

[4]   The angle of incidence in X-ray crystallography is conventionally measured from the plane of reflection rather than from the normal to that plane (as in classical optics). Note t   is just half the angle of deflection of the incident beam (Figure 6.2).

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 $2d \sin \theta$.
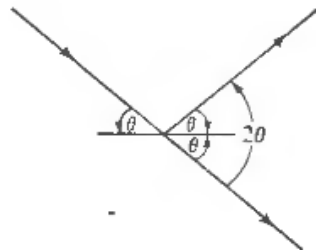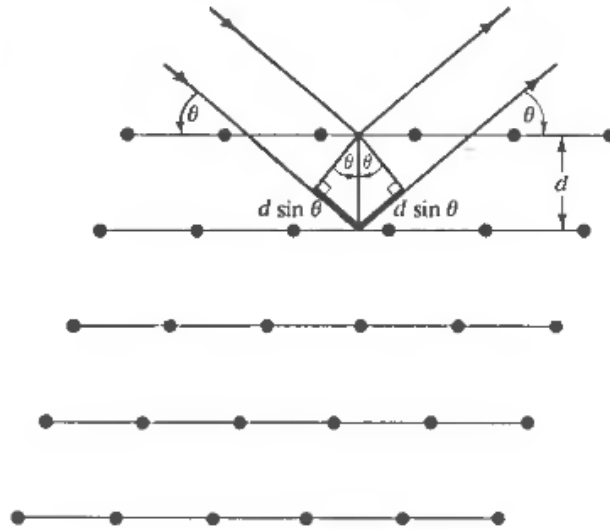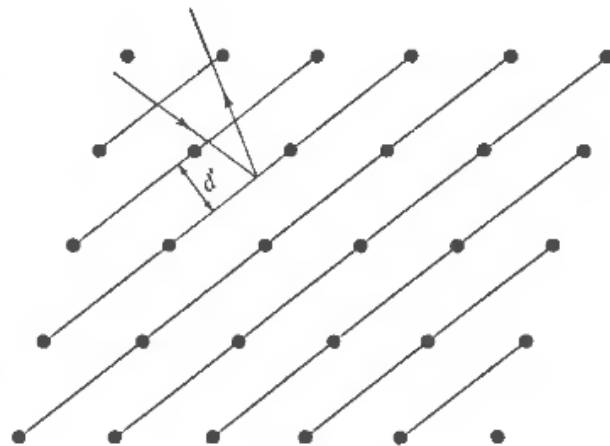
Figure 6.2

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

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.

many different ways of sectioning the crystal into planes, each of which will itself produce further reflections (see, for example, Figure 5.3 or Figure 6.3).

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.[5] Instead one regards the crystal as composed of

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[5] The Bragg assumption of specular reflection is, however, equivalent to the assumption that rays scattered from individual ┆ within each lattice plane interfere constructively. Thus both the Bragg and the von Laue approaches ┆ based on the same physical assumptions, and their precise equivalence (see page 99) is to be expected.
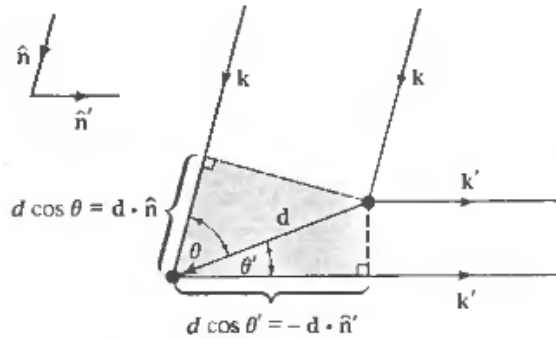
Figure 6.4
Illustrating that the path difference for rays scattered from two points separated by **d** is given by Eq. (6.3) or (6.4).

identical microscopic objects (sets of ions or atoms) placed at the sites **R** of a Bravais lattice, each of which can reradiate the incident radiation in all directions. 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 **d** (Figure 6.4). Let an X ray be incident from very far away, along a direction $\hat{n}$, with wavelength λ, and wave vector $\mathbf{k} = 2\pi\hat{n}/\lambda$. A scattered ray will be observed in a direction $\hat{n}'$ with wavelength[6] λ and wave vector $\mathbf{k}' = 2\pi\hat{n}'/\lambda$, provided that the path difference between the rays scattered by each of the two ions is an integral number of wavelengths. From Figure 6.4 it can be seen that this path difference is just

$$d \cos \theta + d \cos \theta' = \mathbf{d} \cdot (\hat{n} - \hat{n}'). \qquad (6.3)$$

The condition for constructive interference is thus

$$\mathbf{d} \cdot (\hat{n} - \hat{n}') = m\lambda, \qquad (6.4)$$

for integral m. Multiplying both sides of (6.4) by $2\pi/\lambda$ yields a condition on the incident and scattered wave vectors:

$$\mathbf{d} \cdot (\mathbf{k} - \mathbf{k}') = 2\pi m, \qquad (6.5)$$

for integral 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 **R**, the condition that all scattered rays interfere constructively is that condition (6.5) hold simultaneously for all values of **d** that are Bravais lattice vectors:

$$\mathbf{R} \cdot (\mathbf{k} - \mathbf{k}') = 2\pi m, \qquad \text{for integral } m \text{ and all Bravais lattice vectors } \mathbf{R}. \qquad (6.6)$$

This can be written in the equivalent form

$$e^{i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{R}} = 1, \quad \text{for all Bravais lattice vectors } \mathbf{R}. \qquad (6.7)$$

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[6] Here (and in the Bragg picture) we assume that the incident and scattered radiation has the same wavelength. In terms of photons this means that no energy has been lost in the scattering, i.e., that the scattering is elastic. To a good approximation the bulk of the scattered radiation is elastically scattered, though there is much to be learned from the study of that small component of the radiation that is inelastically scattered (Chapter 24 and Appendix N).

Comparing this condition with the definition (5.2) of the reciprocal lattice, we arrive at the Laue condition that *constructive interference will occur provided that the change in wave vector,* $\mathbf{K} = \mathbf{k}' - \mathbf{k}$, *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 $\mathbf{k}$. 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 is

$$k = |\mathbf{k} - \mathbf{K}|. \tag{6.8}$$

Squaring both sides of (6.8) yields the condition

$$\mathbf{k} \cdot \hat{\mathbf{K}} = \tfrac{1}{2}K; \tag{6.9}$$

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 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 k-space to a reciprocal lattice point $\mathbf{K}$ (Figure 6.5). Such k-space planes are called *Bragg planes.*

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 $\mathbf{K}$.
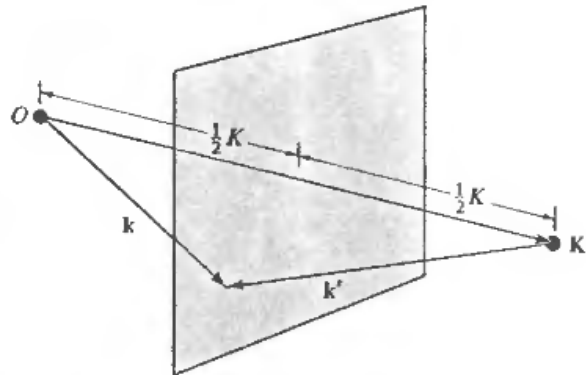
It is a consequence of the equivalence of the Bragg and von Laue points of view, demonstrated in the following section, that the k-space Bragg plane associated with a particular diffraction peak in the Laue formulation is parallel to the family of direct lattice planes responsible for the peak in the Bragg formulation.

EQUIVALENCE OF THE BRAGG AND VON LAUE FORMULATIONS

The equivalence of these two criteria for constructive interference of X rays by a crystal follows from the relation between vectors of the reciprocal lattice and families of direct lattice planes (see Chapter 5). 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,[6] $\mathbf{k}'$ and $\mathbf{k}$ have the same magnitudes. It follows (see Figure 6.6) that $\mathbf{k}'$ and $\mathbf{k}$ make the same angle θ with the plane perpendicular to $\mathbf{K}$. Therefore the scattering can be viewed as a Bragg reflection, with Bragg angle θ, from the family of direct lattice planes perpendicular to the reciprocal lattice vector $\mathbf{K}$.
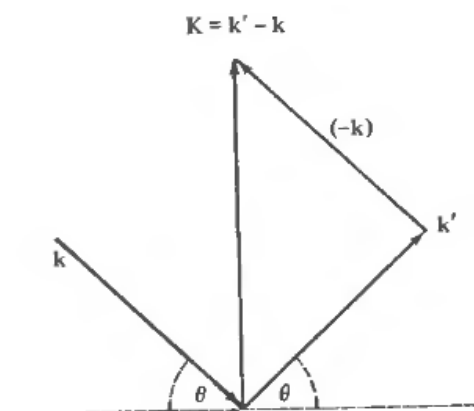
$K = k' - k$

$(-k)$

k'

k

θ θ

Figure 6.6
The plane of the paper contains the incident wave vector **k**, the reflected wave vector **k**', and their difference **K** satisfying the Laue condition. Since the scattering is elastic ($k' = k$), the direction of **K** bisects the angle between **k** and **k**'. The dashed line is the intersection of the plane perpendicular to **K** with the plane of the paper.

To demonstrate that this reflection satisfies the Bragg condition (6.2), note that the vector **K** is an integral multiple[7] of the shortest reciprocal lattice vector K_0 parallel to **K**. According to the theorem on page 90, the magnitude of K_0 is just $2\pi/d$, where d is the distance between successive planes in the family perpendicular to K_0 or to **K**. Thus

$$K = \frac{2\pi n}{d}. \tag{6.10}$$

On the other hand, it follows from Figure 6.6 that $K = 2k \sin \theta$, and thus

$$k \sin \theta = \frac{\pi n}{d}. \tag{6.11}$$

Since $k = 2\pi/\lambda$, Eq. (6.11) implies that the wavelength satisfies the Bragg condition (6.2).

Thus *a Laue diffraction peak corresponding to a change in wave vector given by the reciprocal lattice vector* **K** *corresponds to a Bragg reflection from the family of direct lattice planes perpendicular to* **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**.

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 far more simple to work with than the Bragg condition. In the rest of this chapter we shall 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 information not only about the underlying Bravais lattice, but also about the arrangement of ions within the primitive cell.

EXPERIMENTAL GEOMETRIES SUGGESTED BY THE LAUE CONDITION

An incident wave vector **k** will lead to a diffraction peak (or "Bragg reflection") if and only if the tip of the wave vector lies on a k-space Bragg plane. Since the set of all

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[7] This is an elementary consequence of the fact that the reciprocal lattice is a Bravais lattice. See Chapter 5, Problem 4.

Bragg planes is a discrete family of planes, it cannot begin to fill up three-dimensional k-space, and in general the tip of 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 k, either varying the magnitude of k (i.e., varying the wavelength of the incident beam) or varying its direction (in practice, varying the orientation of the crystal with respect to the incident direction).

The Ewald Construction

A simple geometric construction due to Ewald is of great help in visualizing these various methods and in deducing the crystal structure from the peaks so observed. We draw in k-space a sphere centered on the tip of the incident wave vector k of radius k (so that it passes through the origin). Evidently (see Figure 6.7) there will be *some* wave vector 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.

Figure 6.7
The Ewald construction. Given the incident wave vector k, a sphere of radius k is drawn about the point k. Diffraction peaks corresponding to reciprocal lattice vectors K will be observed only if 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 k' of the Bragg reflected ray.
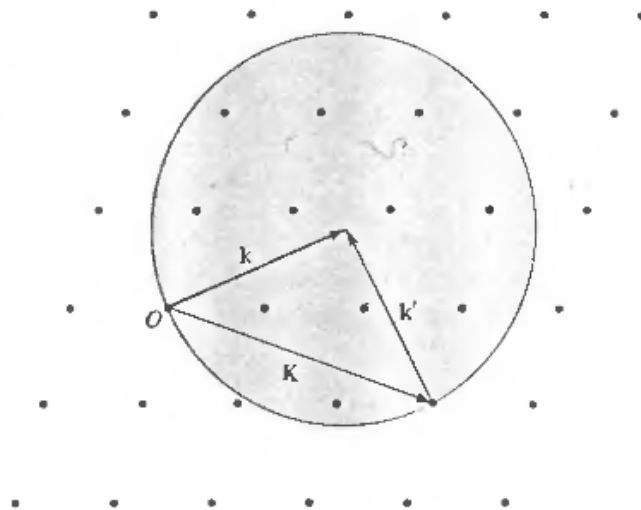
In general, a sphere in k-space with the origin on its surface will have no other reciprocal lattice points on its surface, and therefore the Ewald construction confirms our observation that for a general incident wave vector there will be no Bragg peaks. One can, however, ensure that some Bragg peaks will be produced by several techniques:

1. **The Laue Method**   One can continue to scatter from a single crystal of fixed orientation from a fixed incident direction $\hat{n}$, 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 $k_0 = 2\pi\hat{n}/\lambda_0$ and $k_1 = 2\pi\hat{n}/\lambda_1$, and Bragg peaks will be observed corresponding to any reciprocal lattice vectors lying within this region (Figure 6.8). By making the spread in wavelengths sufficiently large, one
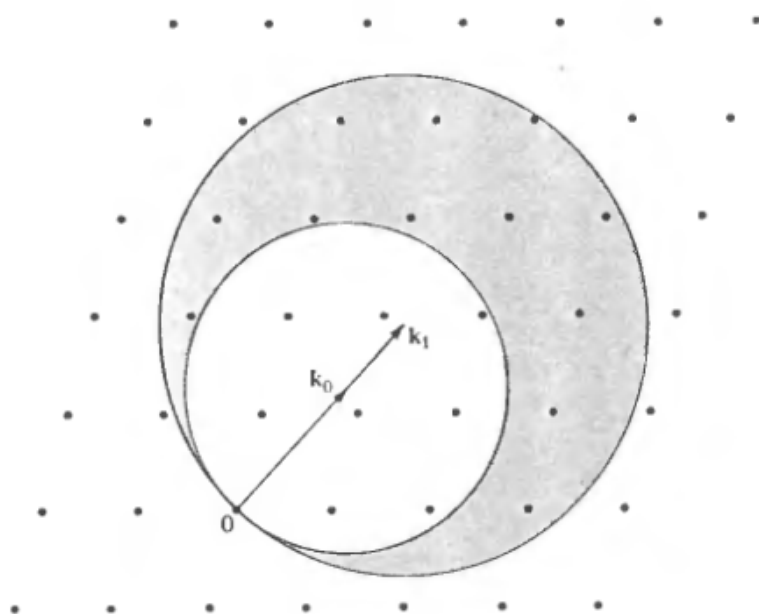
can be sure of finding some reciprocal lattice points within the region; whereas by keeping it from getting too large, one can avoid too many Bragg reflections, thereby keeping the picture fairly simple.

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. Since solid state physicists generally do study substances of known crystal structure, the Laue method is probably the one of greatest practical interest.

2. **The Rotating-Crystal Method**　This method uses monochromatic X rays, but allows the 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 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 **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 traverses a circle about the rotation axis, and a Bragg reflection occurs whenever this circle intersects the Ewald sphere. This is illustrated in Figure 6.9 for a particularly simple geometry.

3. **The Powder or Debye-Scherrer Method**　This is equivalent to a rotating crystal experiment in which, in addition, the axis of rotation is varied over all possible orientations. In practice this isotropic averaging of the incident direction is
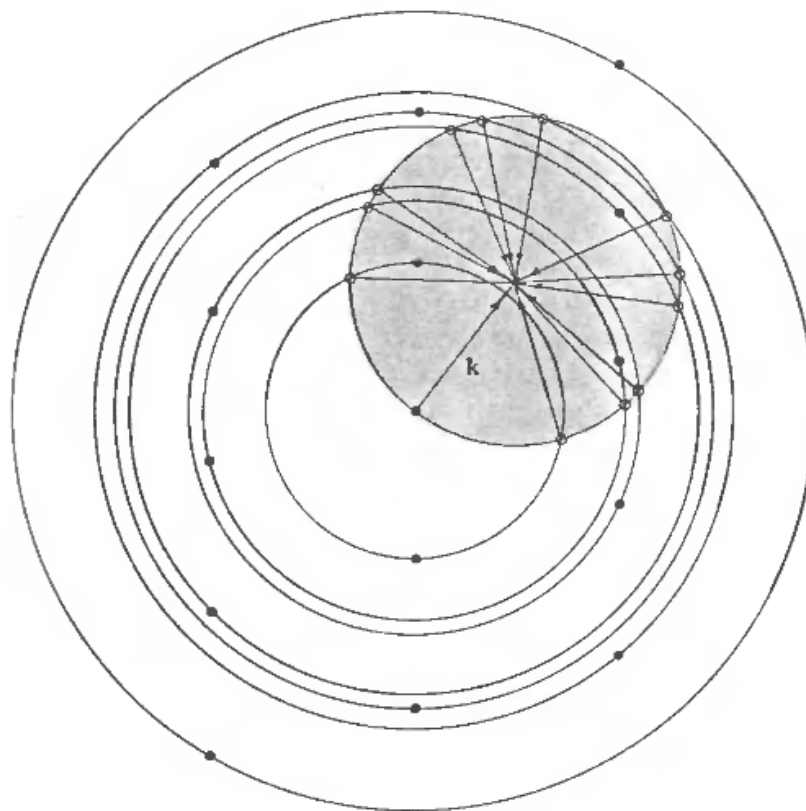
Figure 6.9

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.)

achieved by 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 (Figure 6.10a) provided that K is less than $2k$. 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 (Figure 6.10b)

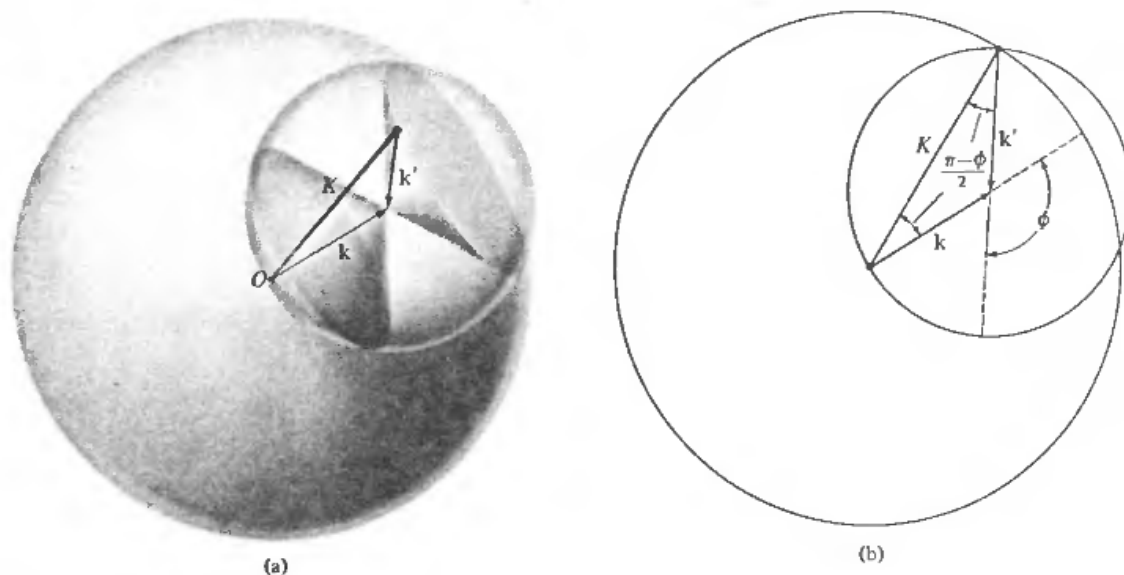$$K = 2k \sin \tfrac{1}{2}\phi. \tag{6.12}$$

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

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 (see, for example, Problem 1).

DIFFRACTION BY A MONATOMIC LATTICE WITH A BASIS; THE GEOMETRICAL STRUCTURE FACTOR

The preceding discussion was based on the condition (6.7) that rays scattered from each primitive cell should interfere constructively. If the crystal structure is that of a monatomic lattice with an n-atom basis (for example, carbon in the diamond structure or hexagonal close-packed beryllium, both of which have $n = 2$), then the contents of each primitive cell can be further analyzed into a set of identical scatterers at positions $\mathbf{d}_1, ..., \mathbf{d}_n$ within the cell. The intensity of radiation in a given Bragg peak will depend on the extent to which the rays scattered from these basis sites interfere with one another, being greatest when there is complete constructive interference and vanishing altogether should there happen to be complete destructive interference.

If the Bragg peak is associated with a change in wave vector $\mathbf{k}' - \mathbf{k} = \mathbf{K}$, then the phase difference (Figure 6.4) between the rays scattered at $\mathbf{d}_i$ and $\mathbf{d}_j$ will be $\mathbf{K} \cdot (\mathbf{d}_i - \mathbf{d}_j)$ and the amplitudes of the two rays will differ by a factor $e^{i\mathbf{K}\cdot(\mathbf{d}_i - \mathbf{d}_j)}$. Thus the amplitudes of the rays scattered at $\mathbf{d}_1, ..., \mathbf{d}_n$ are in the ratios $e^{i\mathbf{K}\cdot\mathbf{d}_1}, \quad e^{i\mathbf{K}\cdot\mathbf{d}_n}$. The net

ray scattered by the entire primitive cell is the sum of the individual rays, and will therefore have an amplitude containing the factor

$$S_K = \sum_{j=1}^{n} e^{i K \cdot d_j}. \tag{6.13}$$

The quantity S_K, known as the *geometrical structure factor*, expresses the extent to which interference of the waves scattered from identical ions within the basis can diminish the intensity of the Bragg peak associated with the reciprocal lattice vector **K**. The intensity in the Bragg peak, being proportional to the square of the absolute value of the amplitude, will contain a factor $|S_K|^2$. It is important to note that this is not the only source of **K** dependence to the intensity. Further dependence on the change in wave vector comes both from the ordinary angular dependence of any electromagnetic scattering, together with the influence on the scattering of the detailed internal structure of each individual ion in the basis. Therefore the structure factor alone cannot be used to predict the absolute intensity in a Bragg peak.[8] It can, however, lead to a characteristic dependence on **K** that is easily discerned even though other less distinctive **K** dependences have been superimposed upon it. The one case, in which the structure factor can be used with assurance is when it vanishes. This occurs when the elements of the basis are so arranged that there is complete destructive interference for the **K** in question; in that case no features of the rays scattered by the individual basis elements can prevent the net ray from vanishing.

We illustrate the importance of a vanishing structure factor in two cases[9]:

1. *Body-Centered Cubic Considered as Simple Cubic with a Basis*   Since the body-centered cubic lattice is a Bravais lattice, we know that Bragg reflections will occur when the change in wave vector **K** is a vector of the reciprocal lattice, which is face-centered cubic. Sometimes, however, it is convenient to regard the bcc lattice as a simple cubic lattice generated by primitive vectors $a\hat{x}$, $a\hat{y}$, and $a\hat{z}$, with a two-point basis consisting of $d_1 = 0$ and $d_2 = (a/2)(\hat{x} + \hat{y} + \hat{z})$. From this point of view the reciprocal lattice is also simple cubic, with a cubic cell of side $2\pi/a$. However, there will now be a structure factor S_K associated with each Bragg reflection. In the present case, (6.13) gives

$$S_K = 1 + \exp\left[i K \cdot \tfrac{1}{2}a(\hat{x} + \hat{y} + \hat{z})\right]. \tag{6.14}$$

A general vector in the simple cubic reciprocal lattice has the form

$$K = \frac{2\pi}{a}(n_1\hat{x} + n_2\hat{y} + n_3\hat{z}). \tag{6.15}$$

Substituting this into (6.14), we find a structure factor

$$\begin{aligned}
S_K &= 1 + e^{i\pi(n_1 + n_2 + n_3)} = 1 + (-1)^{n_1 + n_2 + n_3} \\
&= \begin{cases} 2, & n_1 + n_2 + n_3 \quad \text{even,} \\ 0, & n_1 + n_2 + n_3 \quad \text{odd.} \end{cases}
\end{aligned} \tag{6.16}$$

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[8]   A brief but thorough discussion of the scattering of electromagnetic radiation by crystals, including the derivation of detailed intensity formulas for the various experimental geometries described above, is given by Landau and Lifshitz, *Electrodynamics of Continuous Media*, Chapter 15, Addison-Wesley, Reading, Mass., 1966.

[9]   Further examples are given in Problems 2 and 3.

Thus those points in the simple cubic reciprocal lattice, the sum of whose coordinates with respect to the cubic primitive vectors are odd, will actually have no Bragg reflection associated with them. This converts the simple cubic reciprocal lattice into the face-centered cubic structure that we would have had if we had treated the body-centered cubic direct lattice as a Bravais lattice rather than as a lattice with a basis (see Figure 6.11).
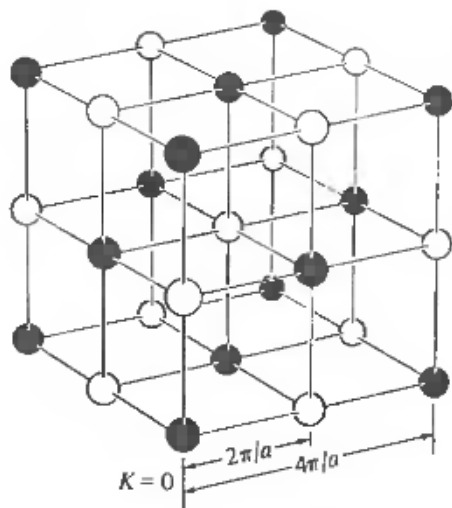
Figure 6.11
Points in the simple cubic reciprocal lattice of side $2\pi/a$, for which the structure factor (6.16) vanishes, are those (white circles) that can be reached from the origin by moving along an odd number of nearest-neighbor bonds. When such sites are eliminated, the remaining sites (black circles) constitute a face-centered cubic lattice with cubic cell of side $4\pi/a$.

Thus if, either inadvertently or for reasons of greater symmetry in description, one chooses to describe a Bravais lattice as a lattice with a basis, one still recovers the correct description of X-ray diffraction, provided that the vanishing of the structure factor is taken into account.

2. *Monatomic Diamond Lattice* The monatomic diamond lattice (carbon, silicon, germanium, or grey tin) is not a Bravais lattice and must be described as a lattice with a basis. The underlying Bravais lattice is face-centered cubic, and the basis can be taken to be $\mathbf{d}_1 = 0$, $\mathbf{d}_2 = (a/4)(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})$, where $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, and $\hat{\mathbf{z}}$, are along the cubic axes and a is the side of the conventional cubic cell. The reciprocal lattice is body-centered cubic with conventional cubic cell of side $4\pi/a$. If we take as primitive vectors

$$\mathbf{b}_1 = \frac{2\pi}{a}(\hat{\mathbf{y}} + \hat{\mathbf{z}} - \hat{\mathbf{x}}), \quad \mathbf{b}_2 = \frac{2\pi}{a}(\hat{\mathbf{z}} + \hat{\mathbf{x}} - \hat{\mathbf{y}}), \quad \mathbf{b}_3 = \frac{2\pi}{a}(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}}), \quad (6.17)$$

then the structure factor (6.13) for $\mathbf{K} = \Sigma n_i \mathbf{b}_i$ is

$$S_{\mathbf{K}} = 1 + \exp\left[\tfrac{1}{2}i\pi(n_1 + n_2 + n_3)\right]$$

$$= \begin{cases} 2, & n_1 + n_2 + n_3 \text{ twice an even number,} \\ 1 \pm i, & n_1 + n_2 + n_3 \text{ odd,} \\ 0, & n_1 + n_2 + n_3 \text{ twice an odd number.} \end{cases} \quad (6.18)$$

To interpret these conditions on Σn_i geometrically, note that if we substitute (6.17) into $\mathbf{K} = \Sigma n_i \mathbf{b}_i$, we can write the general reciprocal lattice vector in the form

$$\mathbf{K} = \frac{4\pi}{a}(v_1 \hat{\mathbf{x}} + v_2 \hat{\mathbf{y}} + v_3 \hat{\mathbf{z}}), \quad (6.19)$$

where

$$v_j = \tfrac{1}{2}(n_1 + n_2 + n_3) - n_j, \quad \sum_{j=1}^{3} v_j = \tfrac{1}{2}(n_1 + n_2 + n_3). \qquad (6.20)$$

We know (see Chapter 5) that the reciprocal to the fcc lattice with cubic cell of side a is a bcc lattice with cubic cell of side $4\pi/a$. Let us regard this as composed of two simple cubic lattices of side $4\pi/a$. The first, containing the origin ($\mathbf{K} = 0$), must have all v_i integers (according to (6.19)) and must therefore be given by $\mathbf{K}$ with $n_1 + n_2 + n_3$ even (according to (6.20)). The second, containing the "body-centered point" $(4\pi/a)\tfrac{1}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})$, must have all v_i integers $+ \tfrac{1}{2}$ (according to (6.19)) and must therefore be given by $\mathbf{K}$ with $n_1 + n_2 + n_3$ odd (according to (6.20)).

Comparing this with (6.18), we find that the points with structure factor $1 \pm i$ are those in the simple cubic sublattice of "body-centered" points. Those whose structure factor S is 2 or 0 are in the simple cubic sublattice containing the origin, where Σv_i is even when $S = 2$ and odd when $S = 0$. Thus the points with zero structure factor are again removed by applying the construction illustrated in Figure 6.11 to the simple cubic sublattice containing the origin, converting it to a face-centered cubic structure (Figure 6.12).

$\bullet \rightarrow S = 2$
$\bullet \rightarrow S = 1 \pm i$
$\bigcirc \rightarrow S = 0$
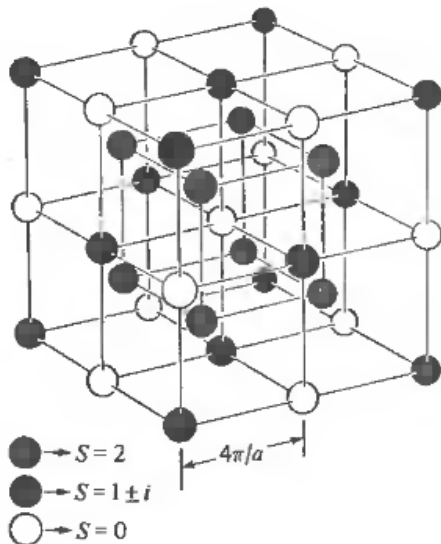
Figure 6.12
The body-centered cubic lattice with cubic cell side $4\pi/a$ that is reciprocal to a face-centered cubic lattice with cubic cell side a. When the fcc lattice is that underlying the diamond structure, then the white circles indicate sites with zero structure factor. (The black circles are sites with structure factor 2, and the gray ones are sites with structure factor $1 \pm i$.)

DIFFRACTION BY A POLYATOMIC CRYSTAL; THE ATOMIC FORM FACTOR

If the ions in the basis are not identical, the structure factor (6.13) assumes the form

$$S_{\mathbf{K}} = \sum_{j=1}^{n} f_j(\mathbf{K})e^{i\mathbf{K} \cdot \mathbf{d}_j}, \qquad (6.21)$$

where f_j, known as the *atomic form factor*, is entirely determined by the internal structure of the ion that occupies position $\mathbf{d}_j$ in the basis. Identical ions have identical form factors (regardless of where they are placed), so (6.21) reduces back to (6.13), multiplied by the common value of the form factors, in the monatomic case.

In elementary treatments the atomic form factor associated with a Bragg reflection

given by the reciprocal lattice vector **K** is taken to be proportional to the Fourier transform of the electronic charge distribution of the corresponding ion[10]:

$$f_j(\mathbf{K}) = -\frac{1}{e} \int d\mathbf{r}\; e^{i\mathbf{K}\cdot\mathbf{r}} \,\rho_j(\mathbf{r}). \tag{6.22}$$

Thus the atomic form factor f_j depends on **K** and on the detailed features of the charge distribution of the ion that occupies position $\mathbf{d}_j$ in the basis. As a result, one would not expect the structure factor to vanish for any **K** unless there is some fortuitous relation between form factors of different types. By making reasonable assumptions about the **K** dependence of the different form factors, one can often distinguish quite conclusively between various possible crystal structures on the basis of the variation with **K** of the Bragg peak intensities (see, for example, Problem 5).

This concludes our discussion of the Bragg reflection of X rays. Our analysis has exploited no properties of the X rays other than their wave nature.[11] Consequently we shall find many of the concepts and results of this chapter reappearing in subsequent discussions of other wave phenomena in solids, such as electrons (Chapter 9) and neutrons (Chapter 24).[12]

PROBLEMS

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1. Powder specimens of three different monatomic cubic crystals are analyzed with a Debye-Scherrer camera. It is known that one sample is face-centered cubic, one is body-centered cubic, and one has the diamond structure. The approximate positions of the first four diffraction rings in each case are (see Figure 6.13):

VALUES OF ϕ FOR SAMPLES

A	B	C
42.2°	28.8°	42.8°
49.2	41.0	73.2
72.0	50.8	89.0
87.3	59.6	115.0

(a) Identify the crystal structures of A, B, and C.

(b) If the wavelength of the incident X-ray beam is 1.5 Å, what is the length of the side of the conventional cubic cell in each case?

(c) If the diamond structure were replaced by a zincblende structure with a cubic unit cell of the same side, at what angles would the first four rings now occur?

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[10]   The electronic charge density $\rho_j(\mathbf{r})$ is that of an ion of type j placed at $\mathbf{r} = 0$; thus the contribution of the ion at $\mathbf{R} + \mathbf{d}_j$ to the electronic charge density of the crystal is $\rho_j(\mathbf{r} - [\mathbf{R} + \mathbf{d}_j])$. (The electronic charge is usually factored out of the atomic form factor to make it dimensionless.)

[11]   As a result we have been unable to make precise statements about the absolute intensity of the Bragg peaks, or about the diffuse background of radiation in directions not allowed by the Bragg condition.

[12]   Considered quantum mechanically, a particle of momentum p can be viewed as a wave of wavelength $\lambda = h/p$.