5
The Reciprocal Lattice

Definitions and Examples
First Brillouin Zone
Lattice Planes and Miller Indices

The reciprocal lattice plays a fundamental role in most analytic studies of periodic structures. One is led to it from such diverse avenues as the theory of crystal diffraction, the abstract study of functions with the periodicity of a Bravais lattice, or the question of what can be salvaged of the law of momentum conservation when the full translational symmetry of free space is reduced to that of a periodic potential. In this brief chapter we shall describe some important elementary features of the reciprocal lattice from a general point of view not tied to any particular application.

DEFINITION OF RECIPROCAL LATTICE

Consider a set of points $\mathbf{R}$ constituting a Bravais lattice, and a plane wave, $e^{i\mathbf{k}\cdot\mathbf{r}}$. For general $\mathbf{k}$, such a plane wave will not, of course, have the periodicity of the Bravais lattice, but for certain special choices of wave vector it will. *The set of all wave vectors* $\mathbf{K}$ *that yield plane waves with the periodicity of a given Bravais lattice is known as its reciprocal lattice.* Analytically, $\mathbf{K}$ belongs to the reciprocal lattice of a Bravais lattice of points $\mathbf{R}$, provided that the relation

$$e^{i\mathbf{K}\cdot(\mathbf{r}+\mathbf{R})} = e^{i\mathbf{K}\cdot\mathbf{r}} \tag{5.1}$$

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

$$e^{i\mathbf{K}\cdot\mathbf{R}} = 1 \tag{5.2}$$

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

Note that a reciprocal lattice is defined with reference to a particular Bravais lattice. The Bravais lattice that determines a given reciprocal lattice is often referred to as the *direct lattice*, when viewed in relation to its reciprocal. Note also that although one could define a set of vectors $\mathbf{K}$ satisfying (5.2) for an arbitrary set of vectors $\mathbf{R}$, such a set of $\mathbf{K}$ is called a reciprocal lattice only if the set of vectors $\mathbf{R}$ is a Bravais lattice.[1]

THE RECIPROCAL LATTICE IS A BRAVAIS LATTICE

That the reciprocal lattice is itself a Bravais lattice follows most simply from the definition of a Bravais lattice given in footnote 7 of Chapter 4, along with the fact that if $\mathbf{K}_1$ and $\mathbf{K}_2$ satisfy (5.2), so, obviously, will their sum and difference.

It is worth considering a more clumsy proof of this fact, which provides an explicit algorithm for constructing the reciprocal lattice. Let $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ be a set of primitive vectors for the direct lattice. Then the reciprocal lattice can be generated by the three primitive vectors

$$\begin{aligned}
\mathbf{b}_1 &= 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}, \\
\mathbf{b}_2 &= 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}, \\
\mathbf{b}_3 &= 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}.
\end{aligned} \tag{5.3}$$

[1] In particular, in working with a lattice with a basis one uses the reciprocal lattice determined by the underlying Bravais lattice, rather than a set of $\mathbf{K}$ satisfying (5.2) for vectors $\mathbf{R}$ describing both the Bravais lattice and the basis points.

To verify that (5.3) gives a set of primitive vectors for the reciprocal lattice, one first notes that the $\mathbf{b}_i$ satisfy[2]

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij}, \tag{5.4}$$

where δ_{ij} is the Kronecker delta symbol:

$$\begin{aligned} \delta_{ij} &= 0, \quad i \neq j; \\ \delta_{ij} &= 1, \quad i = j. \end{aligned} \tag{5.5}$$

Now any vector $\mathbf{k}$ can be written as a linear combination[3] of the $\mathbf{b}_i$:

$$\mathbf{k} = k_1\mathbf{b}_1 + k_2\mathbf{b}_2 + k_3\mathbf{b}_3. \tag{5.6}$$

If $\mathbf{R}$ is any direct lattice vector, then

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3, \tag{5.7}$$

where the n_i are integers. It follows from (5.4) that

$$\mathbf{k} \cdot \mathbf{R} = 2\pi(k_1n_1 + k_2n_2 + k_3n_3). \tag{5.8}$$

For $e^{i\mathbf{k}\cdot\mathbf{R}}$ to be unity for all $\mathbf{R}$ (Eq. (5.2)) $\mathbf{k} \cdot \mathbf{R}$ must be 2π times an integer for any choices of the integers n_i. This requires the coefficients k_i to be integers. Thus the condition (5.2) that $\mathbf{K}$ be a reciprocal lattice vector is satisfied by just those vectors that are linear combinations (5.6) of the $\mathbf{b}_i$ with integral coefficients. Thus (compare Eq. (4.1)) the reciprocal lattice is a Bravais lattice and the $\mathbf{b}_i$ can be taken as primitive vectors.

THE RECIPROCAL OF THE RECIPROCAL LATTICE

Since the reciprocal lattice is itself a Bravais lattice, one can construct *its* reciprocal lattice. This turns out to be nothing but the original direct lattice.

One way to prove this is by constructing $\mathbf{c}_1$, $\mathbf{c}_2$, and $\mathbf{c}_3$ out of the $\mathbf{b}_i$ according to the same formula (5.3) by which the $\mathbf{b}_i$ were constructed from the $\mathbf{a}_i$. It then follows from simple vector identities (Problem 1) that $\mathbf{c}_i = \mathbf{a}_i$, $i = 1, 2, 3$.

A simpler proof follows from the observation that according to the basic definition (5.2), the reciprocal of the reciprocal lattice is the set of all vectors $\mathbf{G}$ satisfying

$$e^{i\mathbf{G}\cdot\mathbf{K}} = 1 \tag{5.9}$$

for all $\mathbf{K}$ in the reciprocal lattice. Since any direct lattice vector $\mathbf{R}$ has this property (again by (5.2)), all direct lattice vectors are in the lattice reciprocal to the reciprocal lattice. Furthermore, no other vectors can be, for a vector not in the direct lattice has the form $\mathbf{r} = x_1\mathbf{a}_1 + x_2\mathbf{a}_2 + x_3\mathbf{a}_3$ with at least one nonintegral x_i. For that value of i, $e^{i\mathbf{b}_i\cdot\mathbf{r}} = e^{2\pi i x_i} \neq 1$, and condition (5.9) is violated for the reciprocal lattice vector $\mathbf{K} = \mathbf{b}_i$.

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[2] When $i \neq j$, Eq. (5.4) follows because the cross product of two vectors is normal to both. When $i = j$, it follows because of the vector identity

$$\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3) = \mathbf{a}_2 \cdot (\mathbf{a}_3 \times \mathbf{a}_1) = \mathbf{a}_3 \cdot (\mathbf{a}_1 \times \mathbf{a}_2).$$

[3] This is t or any three vectors not all in one plane. It is easy to verify that the $\mathbf{b}_i$ are not all in a plane as long as the $\mathbf{a}_i$ are not.

IMPORTANT EXAMPLES

The *simple cubic* Bravais lattice, with cubic primitive cell of side a, has as its reciprocal a simple cubic lattice with cubic primitive cell of side $2\pi/a$. This can be seen, for example, from the construction (5.3), for if

$$\mathbf{a}_1 = a\hat{\mathbf{x}}, \quad \mathbf{a}_2 = a\hat{\mathbf{y}}, \quad \mathbf{a}_3 = a\hat{\mathbf{z}}, \tag{5.10}$$

then

$$\mathbf{b}_1 = \frac{2\pi}{a}\hat{\mathbf{x}}, \quad \mathbf{b}_2 = \frac{2\pi}{a}\hat{\mathbf{y}}, \quad \mathbf{b}_3 = \frac{2\pi}{a}\hat{\mathbf{z}}. \tag{5.11}$$

The *face-centered cubic* Bravais lattice with conventional cubic cell of side a has as its reciprocal a body-centered cubic lattice with conventional cubic cell of side $4\pi/a$. This can be seen by applying the construction (5.3) to the fcc primitive vectors (4.5). The result is

$$\mathbf{b}_1 = \frac{4\pi}{a}\frac{1}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}} - \hat{\mathbf{x}}), \quad \mathbf{b}_2 = \frac{4\pi}{a}\frac{1}{2}(\hat{\mathbf{z}} + \hat{\mathbf{x}} - \hat{\mathbf{y}}), \quad \mathbf{b}_3 = \frac{4\pi}{a}\frac{1}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}}) \tag{5.12}$$

This has precisely the form of the bcc primitive vectors (4.4), provided that the side of the cubic cell is taken to be $4\pi/a$.

The *body-centered cubic* lattice with conventional cubic cell of side a has as its reciprocal a face-centered cubic lattice with conventional cubic cell of side $4\pi/a$. This can again be proved from the construction (5.3), but it also follows from the above result for the reciprocal of the fcc lattice, along with the theorem that the reciprocal of the reciprocal is the original lattice.

It is left as an exercise for the reader to verify (Problem 2) that the reciprocal to a *simple hexagonal* Bravais lattice with lattice constants c and a (Figure 5.1a) is another

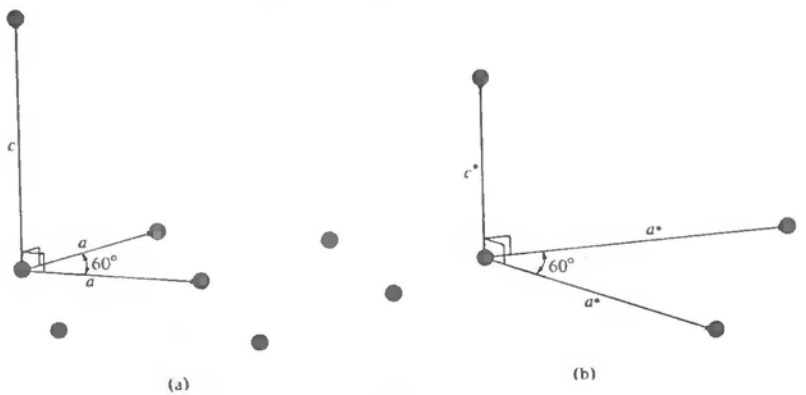


Figure 5.1
(a) Primitive vectors for the simple hexagonal Bravais lattice. (b) Primitive vectors for the lattice reciprocal to that generated by the primitive vectors in (a). The c and c^* axes are parallel. The a^* axes are rotated by 30° with respect to the a axes in the plane perpendicular to the c or c^* axes. The reciprocal lattice is also simple hexagonal.

simple hexagonal lattice with lattice constants $2\pi/c$ and $4\pi/\sqrt{3}a$ (Figure 5.1b), rotated through 30° about the c-axis with respect to the direct lattice.[4]

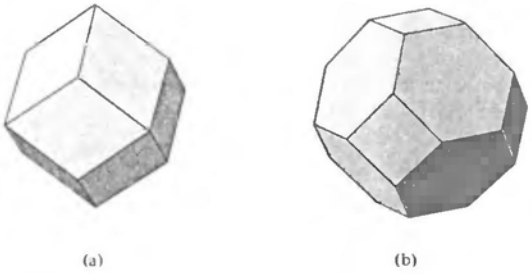
VOLUME OF THE RECIPROCAL LATTICE PRIMITIVE CELL

If v is the volume[5] of a primitive cell in the direct lattice, then the primitive cell of the reciprocal lattice has a volume $(2\pi)^3/v$. This is proved in Problem 1.

FIRST BRILLOUIN ZONE

The Wigner-Seitz primitive cell (page 73) of the reciprocal lattice is known as the *first Brillouin zone*. As the name suggests, one also defines higher Brillouin zones, which are primitive cells of a different type that arise in the theory of electronic levels in a periodic potential. They are described in Chapter 9.

Although the terms "Wigner-Seitz cell" and "first Brillouin zone" refer to identical geometrical constructions, in practice the latter term is applied only to the k-space cell. In particular, when reference is made to the first Brillouin zone of a particular r-space Bravais lattice (associated with a particular crystal structure), what is always meant is the Wigner-Seitz cell of the associated reciprocal lattice. Thus, because the reciprocal of the body-centered cubic lattice is face-centered cubic, the first Brillouin zone of the bcc lattice (Figure 5.2a) is just the fcc Wigner-Seitz cell (Figure 4.16). Conversely, the first Brillouin zone of the fcc lattice (Figure 5.2b) is just the bcc Wigner-Seitz cell (Figure 4.15).



(a) (b)

Figure 5.2
(a) The first Brillouin zone for the body-centered cubic lattice. (b) The first Brillouin zone for the face-centered cubic lattice.

LATTICE PLANES

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

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[4] The hexagonal close-packed *structure* is not a Bravais lattice, and therefore the reciprocal lattice used in the analysis of hcp solids is that of the simple hexagonal lattice (see footnote 1).

[5] The primitive cell volume is independent of the choice of cell, as proved in Chapter 4.

Given a particular Bravais lattice, a *lattice plane* is defined to be any plane containing at least three noncollinear Bravais lattice points. Because of the translational symmetry of the Bravais lattice, any such plane will actually contain infinitely many lattice points, which form a two-dimensional Bravais lattice within the plane. Some lattice planes in a simple cubic Bravais lattice are pictured in Figure 5.3.

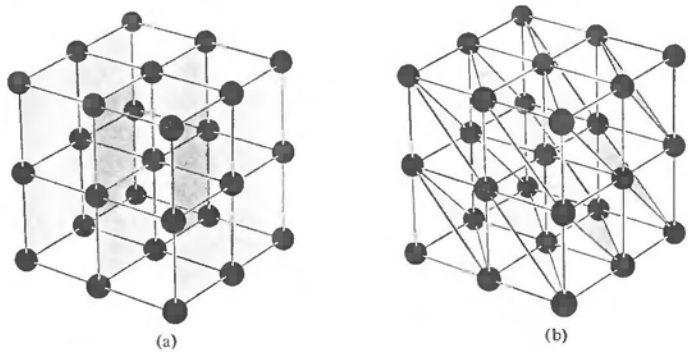

Figure 5.3
Some lattice planes (shaded) in a simple cubic Bravais lattice: (a) and (b) show two different ways of representing the lattice as a family of lattice planes.

By a *family of lattice planes* we mean a set of parallel, equally spaced lattice planes, which together contain all the points of the three-dimensional Bravais lattice. Any lattice plane is a member of such a family. Evidently the resolution of a Bravais lattice into a family of lattice planes is far from unique (Figure 5.3). The reciprocal lattice provides a very simple way to classify all possible families of lattice planes, which is embodied in the following theorem:

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

The theorem is a straightforward consequence of (a) the definition (5.2) of reciprocal lattice vectors as the wave vectors of plane waves that are unity at all Bravais lattice sites and (b) the fact that a plane wave has the same value at all points lying in a family of planes that are perpendicular to its wave vector and separated by an integral number of wavelengths.

To prove the first part of the theorem, given a family of lattice planes, let $\hat{\mathbf{n}}$ be a unit vector normal to the planes. That $\mathbf{K} = 2\pi\hat{\mathbf{n}}/d$ is a reciprocal lattice vector follows from the fact that the plane wave $e^{i\mathbf{K}\cdot\mathbf{r}}$ is constant in planes perpendicular to $\mathbf{K}$ and has the same value in planes separated by $\lambda = 2\pi/K = d$. Since one of the lattice planes contains the Bravais lattice point $\mathbf{r} = \mathbf{0}$, $e^{i\mathbf{K}\cdot\mathbf{r}}$ must be unity for any point $\mathbf{r}$ in any of the planes. Since the planes contain all Bravais lattice points, $e^{i\mathbf{K}\cdot\mathbf{r}} = 1$ for all $\mathbf{R}$, so that $\mathbf{K}$ is indeed a reciprocal lattice vector. Furthermore, $\mathbf{K}$ is the shortest

reciprocal lattice vector normal to the planes, for any wave vector shorter than **K** will give a plane wave with wavelength greater than $2\pi/K = d$. Such a plane wave cannot have the same value on all planes in the family, and therefore cannot give a plane wave that is unity at all Bravais lattice points.

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

MILLER INDICES OF LATTICE PLANES

The correspondence between reciprocal lattice vectors and families of lattice planes provides a convenient way to specify the orientation of a lattice plane. Quite generally one describes the orientation of a plane by giving a vector normal to the plane. Since we know there are reciprocal lattice vectors normal to any family of lattice planes, it is natural to pick a reciprocal lattice vector to represent the normal. To make the choice unique, one uses the shortest such reciprocal lattice vector. In this way one arrives at the *Miller indices* of the plane:

The Miller indices of a lattice plane are the coordinates of the shortest reciprocal lattice vector normal to that plane, with respect to a specified set of primitive reciprocal lattice vectors. Thus a plane with Miller indices h, k, l, is normal to the reciprocal lattice vector $h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$.

As so defined, the Miller indices are integers, since any reciprocal lattice vector is a linear combination of three primitive vectors with integral coefficients. Since the normal to the plane is specified by the shortest perpendicular reciprocal lattice vector, the integers h, k, l can have no common factor. Note also that the Miller indices depend on the particular choice of primitive vectors.

In simple cubic Bravais lattices the reciprocal lattice is also simple cubic and the Miller indices are the coordinates of a vector normal to the plane in the obvious cubic coordinate system. As a general rule, face-centered and body-centered cubic Bravais lattice are described in terms of a conventional cubic cell, i.e., as simple cubic lattices with bases. Since any lattice plane in a fcc or bcc lattice is also a lattice plane in the underlying simple cubic lattice, the same elementary cubic indexing can be used to specify lattice planes. In practice, it is only in the description of noncubic crystals that one must remember that the Miller indices are the coordinates of the normal in a system given by the reciprocal lattice, rather than the direct lattice.

The Miller indices of a plane have a geometrical interpretation in the direct lattice, which is sometimes offered as an alternative way of defining them. Because a lattice

plane with Miller indices h, k, l is perpendicular to the reciprocal lattice vector $\mathbf{K} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$, it will be contained in the continuous plane $\mathbf{K} \cdot \mathbf{r} = A$, for suitable choice of the constant A. This plane intersects the axes determined by the direct lattice primitive vectors $\mathbf{a}_i$ at the points $x_1\mathbf{a}_1$, $x_2\mathbf{a}_2$, and $x_3\mathbf{a}_3$ (Figure 5.4), where the x_i are determined by the condition that $x_i\mathbf{a}_i$ indeed satisfy the equation of the plane: $\mathbf{K} \cdot (x_i\mathbf{a}_i) = A$. Since $\mathbf{K} \cdot \mathbf{a}_1 = 2\pi h$, $\mathbf{K} \cdot \mathbf{a}_2 = 2\pi k$, and $\mathbf{K} \cdot \mathbf{a}_3 = 2\pi l$, it follows that

$$x_1 = \frac{A}{2\pi h}, \quad x_2 = \frac{A}{2\pi k}, \quad x_3 = \frac{A}{2\pi l}. \tag{5.13}$$

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

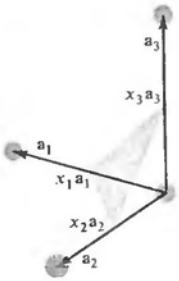

Figure 5.4
An illustration of the crystallographic definition of the Miller indices of a lattice plane. The shaded plane can be a portion of the continuous plane in which the points of the lattice plane lie, or any plane parallel to the lattice plane. The Miller indices are inversely proportional to the x_i.

Crystallographers put the cart before the horse, *defining* the Miller indices to be a set of integers with no common factors, inversely proportional to the intercepts of the crystal plane along the crystal axes:

$$h{:}k{:}l = \frac{1}{x_1}{:}\frac{1}{x_2}{:}\frac{1}{x_3}. \tag{5.14}$$

SOME CONVENTIONS FOR SPECIFYING DIRECTIONS

Lattice planes are usually specified by giving their Miller indices in parentheses: (h, k, l). Thus, in a cubic system, a plane with a normal $(4, -2, 1)$ (or, from the crystallographic viewpoint, a plane with intercepts $(1, -2, 4)$ along cubic axes) is called a $(4, -2, 1)$ plane. The commas are eliminated without confusion by writing $\bar{n}$ instead of $-n$, simplifying the description to $(4\bar{2}1)$. One must know what set of axes is being used to interpret these symbols unambiguously. Simple cubic axes are invariably used when the crystal has cubic symmetry. Some examples of planes in cubic crystals are shown in Figure 5.5.

A similar convention is used to specify directions in the direct lattice, but to avoid confusion with the Miller indices (directions in the reciprocal lattice) square brackets are used instead of parentheses. Thus the body diagonal of a simple cubic lattice lies in the [111] direction and, in general the lattice point $n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$ lies in the direction $[n_1n_2n_3]$ from the origin.

There is also a notation specifying both a family of lattice planes and all those other families that are equivalent to it by virtue of the symmetry of the crystal. Thus

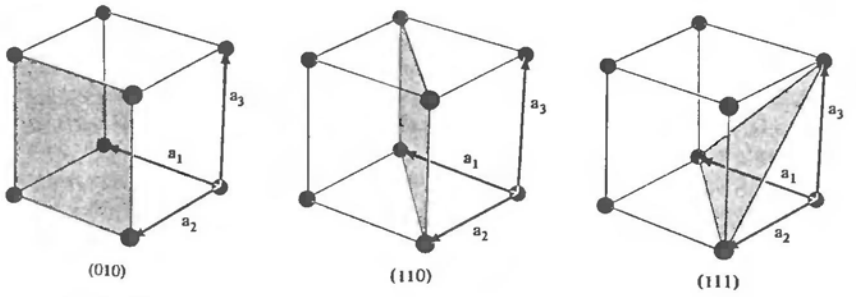

Figure 5.5
Three lattice planes and their Miller indices in a simple cubic Bravais lattice.

the (100), (010), and (001) planes are all equivalent in a cubic crystal. One refers to them collectively as the $\{100\}$ planes, and in general one uses $\{hkl\}$ to refer to the (hkl) planes and all those that are equivalent to them by virtue of the crystal symmetry. A similar convention is used with directions: the [100], [010], [001], $[\bar{1}00]$, $[0\bar{1}0]$, and $[00\bar{1}]$ directions in a cubic crystal are referred to, collectively, as the $\langle 100 \rangle$ directions.

This concludes our general geometrical discussion of the reciprocal lattice. In Chapter 6 we shall see an important example of the utility and the power of the concept in the theory of the diffraction of X rays by a crystal.

PROBLEMS

1. (a) Prove that the reciprocal lattice primitive vectors defined in (5.3) satisfy

$$\mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3) = \frac{(2\pi)^3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}. \tag{5.15}$$

(*Hint:* Write $\mathbf{b}_1$ (but not $\mathbf{b}_2$ or $\mathbf{b}_3$) in terms of the $\mathbf{a}_i$, and use the orthogonality relations (5.4).)

(b) Suppose primitive vectors are constructed from the $\mathbf{b}_i$ in the same manner (Eq. (5.3)) as the $\mathbf{b}_i$ are constructed from the $\mathbf{a}_i$. Prove that these vectors are just the $\mathbf{a}_i$ themselves; i.e., show that

$$2\pi \frac{\mathbf{b}_2 \times \mathbf{b}_3}{\mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3)} = \mathbf{a}_1, \quad \text{etc.} \tag{5.16}$$

(*Hint:* Write $\mathbf{b}_3$ in the numerator (but not $\mathbf{b}_2$) in terms of the $\mathbf{a}_i$, use the vector identity $\mathbf{A} \times (\mathbf{B} \times \mathbf{C}) = \mathbf{B}(\mathbf{A} \cdot \mathbf{C}) - \mathbf{C}(\mathbf{A} \cdot \mathbf{B})$, and appeal to the orthogonality relations (5.4) and the result (5.15) above.)

(c) Prove that the volume of a Bravais lattice primitive cell is

$$v = |\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)|, \tag{5.17}$$

where the $\mathbf{a}_i$ are three primitive vectors. (In conjunction with (5.15) this establishes that the volume of the reciprocal lattice primitive cell is $(2\pi)^3/v$.)

2. (a) Using the primitive vectors given in Eq. (4.9) and the construction (5.3) (or by any other method) show that the reciprocal of the simple hexagonal Bravais lattice is also simple hexagonal, with lattice constants $2\pi/c$ and $4\pi/\sqrt{3}a$, rotated through 30° about the c-axis with respect to the direct lattice.

(b) For what value of c/a does the ratio have the same value in both direct and reciprocal lattices? If c/a is ideal in the direct lattice, what is its value in the reciprocal lattice?

(c) The Bravais lattice generated by three primitive vectors of equal length a, making equal angles θ with one another, is known as the trigonal Bravais lattice (see Chapter 7). Show that the reciprocal of a trigonal Bravais lattice is also trigonal, with an angle θ^* given by $-\cos\theta^* = \cos\theta/[1 + \cos\theta]$, and a primitive vector length a^*, given by $a^* = (2\pi/a)(1 + 2\cos\theta\cos\theta^*)^{-1/2}$.

3. (a) Show that the density of lattice points (per unit area) in a lattice plane is d/v, where v is the primitive cell volume and d the spacing between neighboring planes in the family to which the given plane belongs.

(b) Prove that the lattice planes with the greatest densities of points are the $\{111\}$ planes in a face-centered cubic Bravais lattice and the $\{110\}$ planes in a body-centered cubic Bravais lattice. (*Hint:* This is most easily done by exploiting the relation between families of lattice planes and reciprocal lattice vectors.)

4. Prove that any reciprocal lattice vector $\mathbf{K}$ is an integral multiple of the shortest parallel reciprocal lattice vector $\mathbf{K}_0$. (Hint: Assume the contrary, and deduce that since the reciprocal lattice is a Bravais lattice, there must be a reciprocal lattice vector parallel to $\mathbf{K}$ shorter than $\mathbf{K}_0$.)

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 that θ is just half the angle of deflection of the incident beam (Figure 6.2).

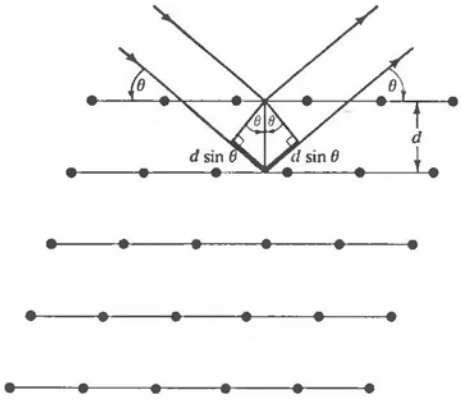

Figure 6.1
A Bragg reflection from a particular family of lattice planes, separated by a distance d. Incident and reflected rays are shown for the two neighboring planes. The path difference is $2d \sin \theta$.

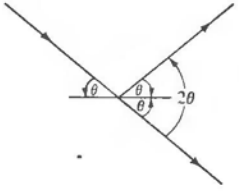

Figure 6.2
The Bragg angle θ is just half the total angle by which the incident beam is deflected.

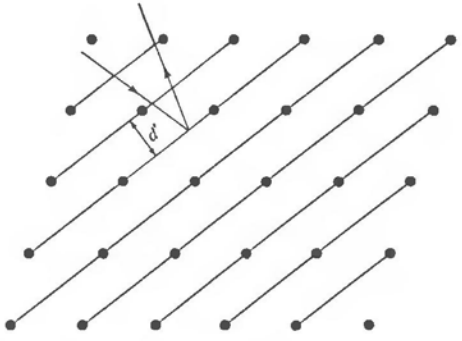

Figure 6.3
The same portion of Bravais lattice shown in Figure 6.1, with a different resolution into lattice planes indicated. The incident ray is the same as in Figure 6.1, but both the direction (shown in the figure) and wavelength (determined by the Bragg condition (6.2) with d replaced by d') of 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

[5] The Bragg assumption of specular reflection is, however, equivalent to the assumption that rays scattered from individual [illegible] within each lattice plane interfere constructively. Thus both the Bragg and the von Laue approaches [illegible] based on the same physical assumptions, and their precise equivalence (see page 99) is to be expected.

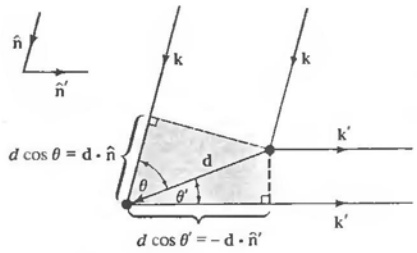

Figure 6.4
Illustrating that the path difference for rays scattered from two points separated by **d** is given by Eq. (6.3) or (6.4).

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 $\hat{\mathbf{n}}$, with wavelength λ, and wave vector $\mathbf{k} = 2\pi\hat{\mathbf{n}}/\lambda$. A scattered ray will be observed in a direction $\hat{\mathbf{n}}'$ with wavelength[6] λ and wave vector $\mathbf{k}' = 2\pi\hat{\mathbf{n}}'/\lambda$, 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

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

The condition for constructive interference is thus

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

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

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

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:

$$\mathbf{R}\cdot(\mathbf{k} - \mathbf{k}') = 2\pi m, \quad \begin{array}{l}\text{for integral } m \text{ and}\\ \text{all Bravais lattice}\\ \text{vectors } \mathbf{R}.\end{array} \tag{6.6}$$

This can be written in the equivalent form

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

---

[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.*

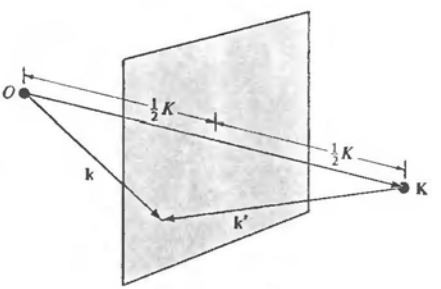

Figure 6.5
The Laue condition. If the sum of $\mathbf{k}$ and $-\mathbf{k}'$ is a vector $\mathbf{K}$, and if $\mathbf{k}$ and $\mathbf{k}'$ have the same length, then the tip of the vector $\mathbf{k}$ is equidistant from the origin O and the tip of the vector $\mathbf{K}$, and therefore it lies in 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 $\mathbf{K}$.

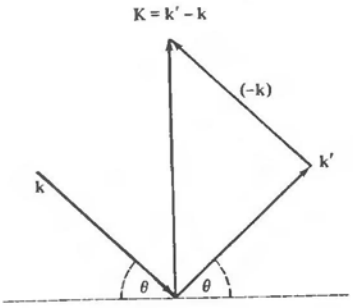

Figure 6.6
The plane of the paper contains the incident wave vector **k**, the reflected wave vector **k′**, and their difference **K** satisfying the Laue condition. Since the scattering is elastic ($k' = k$), the direction of **K** bisects the angle between **k** and **k′**. The dashed line is the 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 $\mathbf{K}_0$ parallel to **K**. According to the theorem on page 90, the magnitude of $\mathbf{K}_0$ is just $2\pi/d$, where d is the distance between successive planes in the family perpendicular to $\mathbf{K}_0$ or to **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

[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 $\mathbf{k}$ will not lie on a Bragg plane. Thus for a fixed incident wave vector—i.e., for a fixed X-ray wavelength and fixed incident direction relative to the crystal axes—there will be in general no diffraction peaks at all.

If one wishes to search experimentally for Bragg peaks one must therefore relax the constraint of fixed $\mathbf{k}$, either varying the magnitude of $\mathbf{k}$ (i.e., varying the wavelength of the incident beam) or varying its direction (in practice, varying the orientation of the crystal 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 $\mathbf{k}$ of radius k (so that it passes through the origin). Evidently (see Figure 6.7) there will be *some* wave vector $\mathbf{k}'$ satisfying the Laue condition if and only if some reciprocal lattice point (in addition to the origin) lies on the surface of the sphere, in which case there will be a Bragg reflection from the family of direct lattice planes perpendicular to that reciprocal lattice vector.

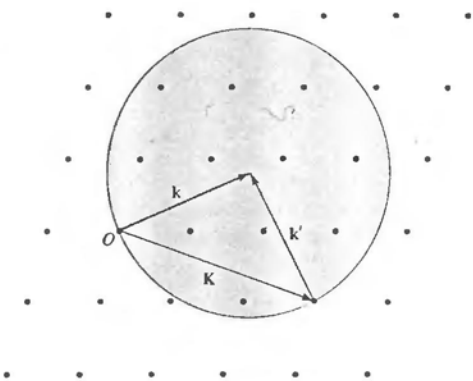

Figure 6.7
The Ewald construction. Given the incident wave vector $\mathbf{k}$, a sphere of radius k is drawn about the point $\mathbf{k}$. Diffraction peaks corresponding to reciprocal lattice vectors $\mathbf{K}$ will be observed only if $\mathbf{K}$ gives a reciprocal lattice point on the surface of the sphere. Such a reciprocal lattice vector is indicated in the figure, together with the wave vector $\mathbf{k}'$ of the Bragg reflected ray.

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

1. **The Laue Method** One can continue to scatter from a single crystal of fixed orientation from a fixed incident direction $\hat{\mathbf{n}}$, but can search for Bragg peaks by using not a monochromatic X-ray beam, but one containing wavelengths from λ_1 up to λ_0. The Ewald sphere will then expand into the region contained between the two spheres determined by $\mathbf{k}_0 = 2\pi\hat{\mathbf{n}}/\lambda_0$ and $\mathbf{k}_1 = 2\pi\hat{\mathbf{n}}/\lambda_1$, and Bragg peaks will be observed corresponding to any reciprocal lattice vectors lying within this region (Figure 6.8). By making the spread in wavelengths sufficiently large, one

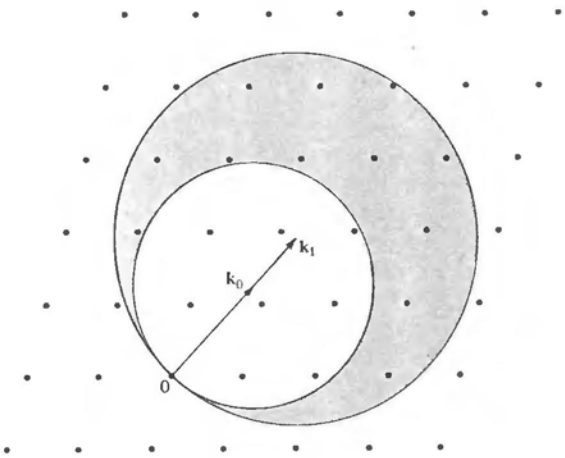

Figure 6.8
The Ewald construction for the Laue method. The crystal and incident X-ray direction are fixed, and a continuous range of wavelengths, corresponding to wave vectors between k_0 and k_1 in magnitude, is present. The Ewald spheres for all incident wave vectors fill the shaded region between the sphere centered on the tip of the vector $\mathbf{k}_0$ and that centered on the tip of $\mathbf{k}_1$. Bragg peaks will be observed corresponding to all reciprocal lattice points lying within the shaded region. (For simplicity in illustration, the incident direction has been taken to lie in a lattice plane, and only reciprocal lattice points lying in that plane are shown.)

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 $\mathbf{k}$) is fixed in k-space, while the entire reciprocal lattice rotates about the axis of rotation of the crystal. During this rotation each reciprocal lattice point 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

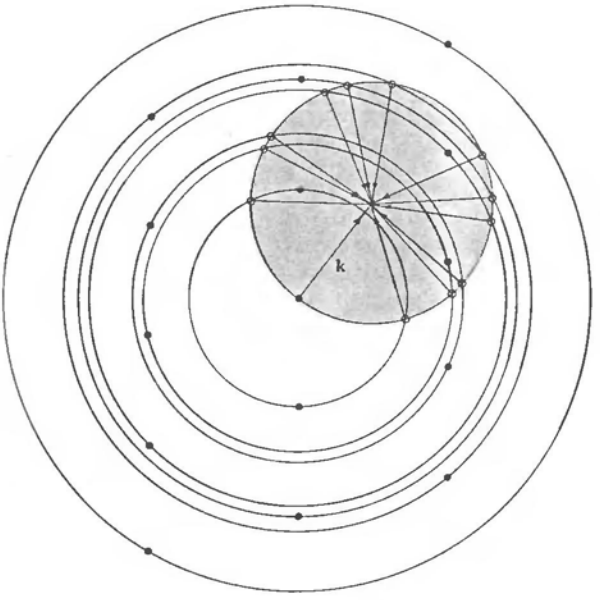

Figure 6.9
The Ewald construction for the rotating-crystal method. For simplicity a case is shown in which the incident wave vector lies in a lattice plane, and the axis of rotation is perpendicular to that plane. The concentric circles are the orbits swept out under the rotation by the reciprocal lattice 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)

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

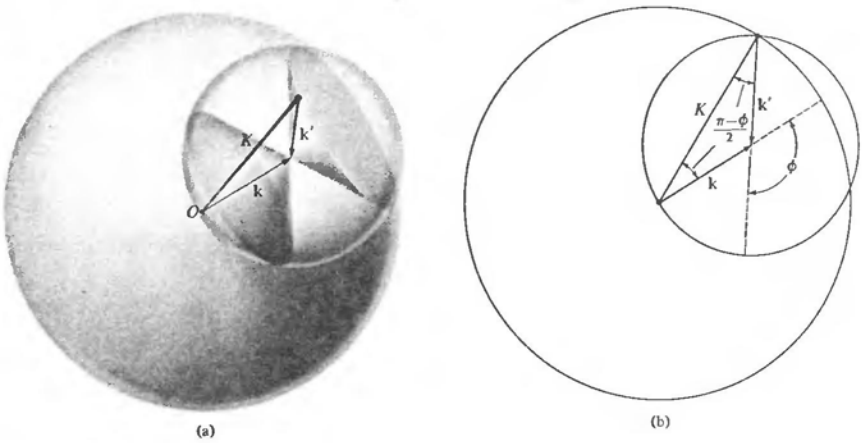

Figure 6.10
The Ewald construction for the powder method. (a) The Ewald sphere is the smaller sphere. It is centered on the tip of the incident wave vector $\mathbf{k}$ with radius k, so that the origin O is on its surface. The larger sphere is centered on the origin and has a radius K. The two spheres intersect in a circle (foreshortened to an ellipse). Bragg reflections will occur for any wave vector $\mathbf{k}'$ connecting any point on the circle of intersection to the tip of the vector $\mathbf{k}$. The scattered rays therefore lie on the cone that opens in the direction opposite to $\mathbf{k}$. (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 $\mathbf{d}_1, \ldots, \mathbf{d}_n$ 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 $\mathbf{d}_1, \ldots, \mathbf{d}_n$ 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

$$S_{\mathbf{K}} = \sum_{j=1}^{n} e^{i\mathbf{K}\cdot\mathbf{d}_j}. \tag{6.13}$$

The quantity $S_{\mathbf{K}}$, 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 $\mathbf{K}$. The intensity in the Bragg peak, being proportional to the square of the absolute value of the amplitude, will contain a factor $|S_{\mathbf{K}}|^2$. It is important to note that this is not the only source of $\mathbf{K}$ 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 $\mathbf{K}$ that is easily discerned even though other less distinctive $\mathbf{K}$ 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 $\mathbf{K}$ 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 $\mathbf{K}$ 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 $a\hat{\mathbf{x}}$, $a\hat{\mathbf{y}}$, and $a\hat{\mathbf{z}}$, with a two-point basis consisting of $\mathbf{d}_1 = 0$ and $\mathbf{d}_2 = (a/2)(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})$. 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 $S_{\mathbf{K}}$ associated with each Bragg reflection. In the present case, (6.13) gives

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

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

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

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

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

---

[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).

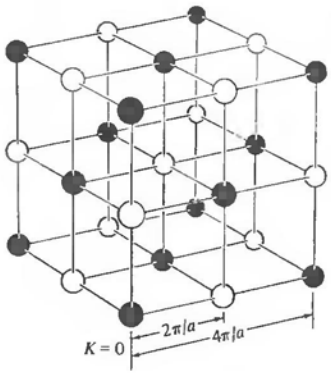

Figure 6.11
Points in the simple cubic reciprocal lattice of side $2\pi/a$, for which the structure factor (6.16) vanishes, are those (white circles) that can be reached from the origin by moving along an odd number of nearest-neighbor bonds. When such sites are eliminated, the remaining sites (black 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

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

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

$$\begin{aligned} S_{\mathbf{K}} &= 1 + \exp\left[\tfrac{1}{2}i\pi(n_1 + n_2 + n_3)\right] \\ &= \begin{cases} 2, & n_1 + n_2 + n_3 \text{ twice an even number,} \\ 1 \pm i, & n_1 + n_2 + n_3 \text{ odd,} \\ 0, & n_1 + n_2 + n_3 \text{ twice an odd number.} \end{cases} \end{aligned} \tag{6.18}$$

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

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

where

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

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" $(4\pi/a)\frac{1}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})$, must have all v_i integers $+ \frac{1}{2}$ (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).

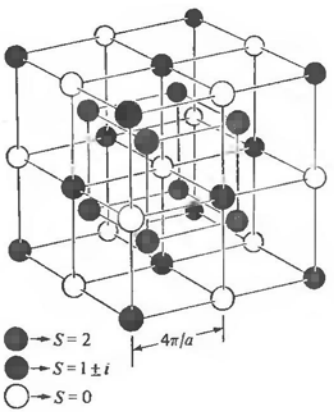

Figure 6.12
The body-centered cubic lattice with cubic cell side $4\pi/a$ that is reciprocal to a face-centered cubic lattice with cubic cell side a. When the fcc lattice is that underlying the diamond structure, then the white circles indicate sites with zero structure factor. (The black circles are 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

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

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 $\mathbf{K}$ 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 $\mathbf{K}$ 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 $\mathbf{K}$ unless there is some fortuitous relation between form factors of different types. By making reasonable assumptions about the $\mathbf{K}$ dependence of the different form factors, one can often distinguish quite conclusively between various possible crystal structures on the basis of the variation with $\mathbf{K}$ 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

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?

[10] The electronic charge density $\rho_j(\mathbf{r})$ is that of an ion of type j placed at $\mathbf{r} = \mathbf{0}$; 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 $\lambda = h/p$.

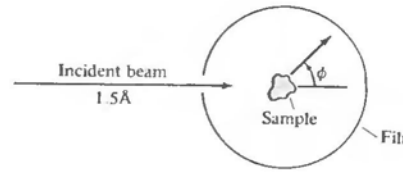

Figure 6.13
Schematic view of a Debye-Scherrer camera. Diffraction peaks are recorded on the film strip.

2. It is often convenient to represent a face-centered cubic Bravais lattice as simple cubic, with a cubic primitive cell of side a and a four-point basis.

(a) Show that the structure factor (6.13) is then either 4 or 0 at all points of the simple cubic reciprocal lattice.

(b) Show that when points with zero structure factor are removed, the remaining points of the reciprocal lattice make up a body-centered cubic lattice with conventional cell of side $4\pi/a$. Why is this to be expected?

3. (a) Show that the structure factor for a monatomic hexagonal close-packed crystal structure can take on any of the six values $1 + e^{in\pi/3}$, $n = 1, \ldots, 6$, as $\mathbf{K}$ ranges through the points of the simple hexagonal reciprocal lattice.

(b) Show that all reciprocal lattice points have nonvanishing structure factor in the plane perpendicular to the c-axis containing $\mathbf{K} = \mathbf{0}$.

(c) Show that points of zero structure factor are found in alternate planes in the family of reciprocal lattice planes perpendicular to the c-axis.

(d) Show that in such a plane the point that is displaced from $\mathbf{K} = \mathbf{0}$ by a vector parallel to the c-axis has zero structure factor.

(e) Show that the removal of all points of zero structure factor from such a plane reduces the triangular network of reciprocal lattice points to a honeycomb array (Figure 4.3).

4. Consider a lattice with an n-ion basis. Suppose that the ith ion in the basis, when translated to $\mathbf{r} = 0$, can be regarded as composed of m_i point particles of charge $-z_{ij}e$, located at positions $\mathbf{b}_{ij}, j = 1, \ldots, m_i$.

(a) Show that the atomic form factor f_i is given by

$$f_i = \sum_{j=1}^{m_i} z_{ij} e^{i\mathbf{K}\cdot\mathbf{b}_{ij}}. \tag{6.23}$$

(b) Show that the total structure factor (6.21) implied by (6.23) is identical to the structure factor one would have found if the lattice were equivalently described as having a basis of $m_1 + \cdots + m_n$ point ions.

5. (a) The sodium chloride structure (Figure 4.24) can be regarded as an fcc Bravais lattice of cube side a, with a basis consisting of a positively charged ion at the origin and a negatively charged ion at $(a/2)\hat{\mathbf{x}}$. The reciprocal lattice is body-centered cubic, and the general reciprocal lattice vector has the form (6.19), with all the coefficients ν_i either integers or integers $+\frac{1}{2}$. If the atomic form factors for the two ions are f_+ and f_-, show that the structure factor is $S_{\mathbf{K}} = f_+ + f_-$, if the ν_i are integers, and $f_+ - f_-$, if the ν_i are integers $+\frac{1}{2}$. (Why does S vanish in the latter case when $f_+ = f_-$?)

(b) The zincblende structure (Figure 4.18) is also a face-centered cubic Bravais lattice of cube side a, with a basis consisting of a positively charged ion at the origin and a negatively charged

ion at $(a/4)(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})$. Show that the structure factor $S_{\mathbf{K}}$ is $f_+ \pm if_-$ if the v_i are integers $+\frac{1}{2}$, $f_+ + f_-$ if the v_i are integers and Σv_i is even, and $f_+ - f_-$ if the v_i are integers and Σv_i is odd.

(c) Suppose that a cubic crystal is known to be composed of closed-shell (and hence spherically symmetric) ions, so that $f_\pm(\mathbf{K})$ depends only on the magnitude of $\mathbf{K}$. The positions of the Bragg peaks reveal that the Bravais lattice is face-centered cubic. Discuss how one might determine, from the structure factors associated with the Bragg peaks, whether the crystal structure was likely to be of the sodium chloride or zincblende type.