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Basic Aspects of X-Ray Diffraction

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Basic Aspects of X-Ray Diffraction

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pation of heat by water-cooling, conduction, radiation, etc., how long would it take a 100-gm copper target to melt? (Melting point of copper = 1083°C, mean specific heat = 6.65 cal/mole/°C, latent heat of fusion = 3,220 cal/mole.)

1–18. Assume that the sensitivity of x-ray film is proportional to the mass absorption coefficient of the silver bromide in the emulsion for the particular wavelength involved. What, then, is the ratio of film sensitivities to Cu $K\alpha$ and Mo $K\alpha$ radiation?

CHAPTER 2

THE GEOMETRY OF CRYSTALS

2–1 Introduction. Turning from the properties of x-rays, we must now consider the geometry and structure of crystals in order to discover what there is about crystals in general that enables them to diffract x-rays. We must also consider particular crystals of various kinds and how the very large number of crystals found in nature are classified into a relatively small number of groups. Finally, we will examine the ways in which the orientation of lines and planes in crystals can be represented in terms of symbols or in graphical form.

A crystal may be defined as *a solid composed of atoms arranged in a pattern periodic in three dimensions*. As such, crystals differ in a fundamental way from gases and liquids because the atomic arrangements in the latter do not possess the essential requirement of periodicity. Not all solids are crystalline, however; some are *amorphous*, like glass, and do not have any regular interior arrangement of atoms. There is, in fact, no essential difference between an amorphous solid and a liquid, and the former is often referred to as an "undercooled liquid."

2–2 Lattices. In thinking about crystals, it is often convenient to ignore the actual atoms composing the crystal and their periodic arrangement in space, and to think instead of a set of imaginary points which has a fixed relation in space to the atoms of the crystal and may be regarded as a sort of framework or skeleton on which the actual crystal is built up.

This set of points can be formed as follows. Imagine space to be divided by three sets of planes, the planes in each set being parallel and equally spaced. This division of space will produce a set of cells each identical in size, shape, and orientation to its neighbors. Each cell is a parallelepiped, since its opposite faces are parallel and each face is a parallelogram. The space-dividing planes will intersect each other in a set of lines (Fig. 2–1), and these lines in turn intersect in the set of points referred to above. A set of points so formed has an important property: it constitutes a *point lattice*, which is defined as *an array of points in space so arranged that each point has identical surroundings*. By "identical surroundings" we mean that the lattice of points, when viewed in a particular direction from one lattice point, would have exactly the same appearance when viewed in the same direction from any other lattice point.

Since all the cells of the lattice shown in Fig. 2–1 are identical, we may choose any one, for example the heavily outlined one, as a *unit cell*. The

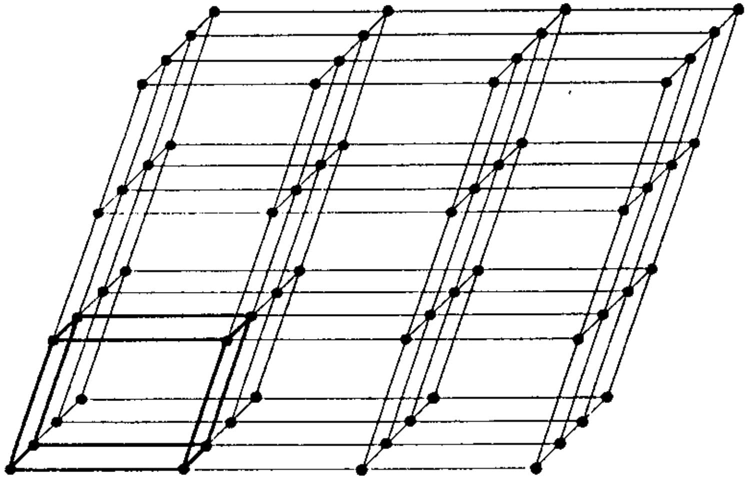

FIG. 2-1. A point lattice.

size and shape of the unit cell can in turn be described by the three vectors* **a**, **b**, and **c** drawn from one corner of the cell taken as origin (Fig. 2-2). These vectors define the cell and are called the *crystallographic axes* of the cell. They may also be described in terms of their lengths (a, b, c) and the angles between them (α, β, γ). These lengths and angles are the *lattice constants* or *lattice parameters* of the unit cell.

Note that the vectors **a**, **b**, **c** define, not only the unit cell, but also the whole point lattice through the translations provided by these vectors. In other words, the whole set of points in the lattice can be produced by repeated action of the vectors **a**, **b**, **c** on one lattice point located at the origin, or, stated alternatively, the vector coordinates of any point in the lattice are P**a**, Q**b**, and R**c**, where P, Q, and R are whole numbers. It follows that the arrangement of points in a point lattice is absolutely periodic in three dimensions, points being repeated at regular intervals along any line one chooses to draw through the lattice.

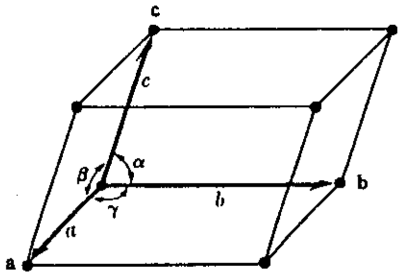

FIG. 2-2. A unit cell.

2-3 Crystal systems.

In dividing space by three sets of planes, we can of course produce unit cells of various shapes, depending on how we arrange the planes. For example, if the planes in the three sets are all equally

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* Vectors are here represented by boldface symbols. The same symbol in italics stands for the absolute value of the vector.

TABLE 2-1

CRYSTAL SYSTEMS AND BRAVAIS LATTICES

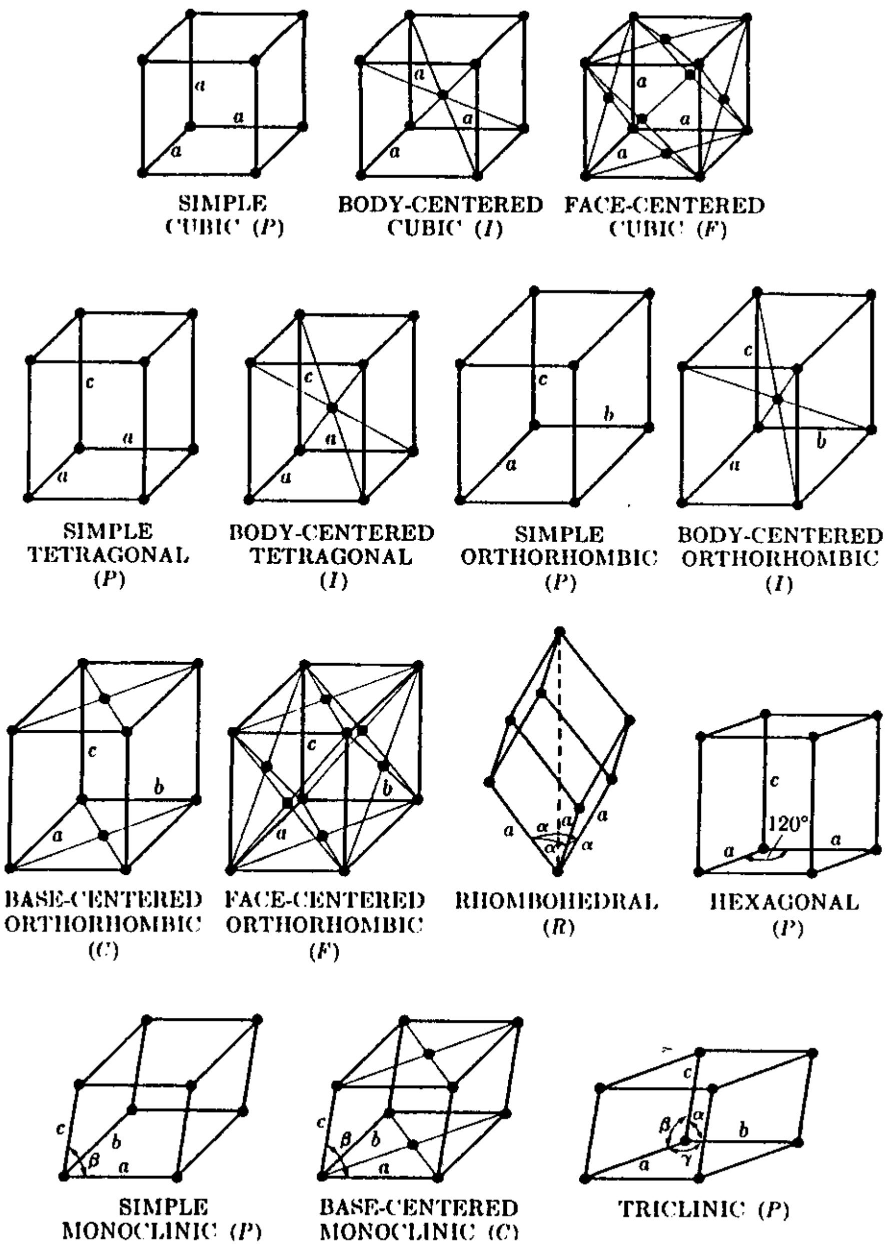
(The symbol ≠ implies nonequality by reason of symmetry. Accidental equality may occur, as shown by an example in Sec. 2-4.)

System	Axials lengths and angles	Bravais lattice	Lattice symbol
Cubic	Three equal axes at right angles $a = b = c$, $\alpha = \beta = \gamma = 90°$	Simple Body-centered Face-centered	P I F
Tetragonal	Three axes at right angles, two equal $a = b \neq c$, $\alpha = \beta = \gamma = 90°$	Simple Body-centered	P I
Orthorhombic	Three unequal axes at right angles $a \neq b \neq c$, $\alpha = \beta = \gamma = 90°$	Simple Body-centered Base-centered Face-centered	P I C F
Rhombohedral*	Three equal axes, equally inclined $a = b = c$, $\alpha = \beta = \gamma \neq 90°$	Simple	R
Hexagonal	Two equal coplanar axes at 120°, third axis at right angles $a = b \neq c$, $\alpha = \beta = 90°$, $\gamma = 120°$	Simple	P
Monoclinic	Three unequal axes, one pair not at right angles $a \neq b \neq c$, $\alpha = \gamma = 90° \neq \beta$	Simple Base-centered	P C
Triclinic	Three unequal axes, unequally inclined and none at right angles $a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90°$	Simple	P

* Also called trigonal.

spaced and mutually perpendicular, the unit cell is cubic. In this case the vectors **a**, **b**, **c** are all equal and at right angles to one another, or $a = b = c$ and $\alpha = \beta = \gamma = 90°$. By thus giving special values to the axial lengths and angles, we can produce unit cells of various shapes and therefore various kinds of point lattices, since the points of the lattice are located at the cell corners. It turns out that only seven different kinds of cells are necessary to include all the possible point lattices. These correspond to the seven *crystal systems* into which all crystals can be classified. These systems are listed in Table 2-1.

Seven different point lattices can be obtained simply by putting points at the corners of the unit cells of the seven crystal systems. However, there are other arrangements of points which fulfill the requirements of a point lattice, namely, that each point have identical surroundings. The French crystallographer Bravais worked on this problem and in 1848 demonstrated that there are fourteen possible point lattices and no more; this important result is commemorated by our use of the terms *Bravais*



SIMPLE CUBIC (P)
BODY-CENTERED CUBIC (I)
FACE-CENTERED CUBIC (F)
SIMPLE TETRAGONAL (P)
BODY-CENTERED TETRAGONAL (I)
SIMPLE ORTHORHOMBIC (P)
BODY-CENTERED ORTHORHOMBIC (I)
BASE-CENTERED ORTHORHOMBIC (C)
FACE-CENTERED ORTHORHOMBIC (F)
RHOMBOHEDRAL (R)
HEXAGONAL (P)
SIMPLE MONOCLINIC (P)
BASE-CENTERED MONOCLINIC (C)
TRICLINIC (P)

Fig. 2-3. The fourteen Bravais lattices.

lattice and *point lattice* as synonymous. For example, if a point is placed at the center of each cell of a cubic point lattice, the new array of points

on a cubic unit cell having lattice points at each corner and in the center of each face.

The fourteen Bravais lattices are described in Table 2-1 and illustrated in Fig. 2-3, where the symbols P, F, I, etc., have the following meanings. We must first distinguish between *simple*, or *primitive*, cells (symbol P or R) and *nonprimitive* cells (any other symbol): primitive cells have only one lattice point per cell while nonprimitive have more than one. A lattice point in the interior of a cell "belongs" to that cell, while one in a cell face is shared by two cells and one at a corner is shared by eight. The number of lattice points per cell is therefore given by

$$N = N_i + \frac{N_f}{2} + \frac{N_c}{8}, \qquad (2\text{-}1)$$

where N_i = number of interior points, N_f = number of points on faces, and N_c = number of points on corners. Any cell containing lattice points on the corners only is therefore primitive, while one containing additional points in the interior or on faces is nonprimitive. The symbols F and I refer to face-centered and body-centered cells, respectively, while A, B, and C refer to base-centered cells, centered on one pair of opposite faces A, B, or C. (The A face is the face defined by the b and c axes, etc.) The symbol R is used especially for the rhombohedral system. In Fig. 2-3, axes of equal length in a particular system are given the same symbol to indicate their equality, e.g., the cubic axes are all marked a, the two equal tetragonal axes are marked a and the third one c, etc.

At first glance, the list of Bravais lattices in Table 2-1 appears incomplete. Why not, for example, a base-centered tetragonal lattice? The full lines in Fig. 2-4 delineate such a cell, centered on the C face, but we see that the same array of lattice points can be referred to the simple tetragonal cell shown by dashed lines, so that the base-centered arrangement of points is not a new lattice.

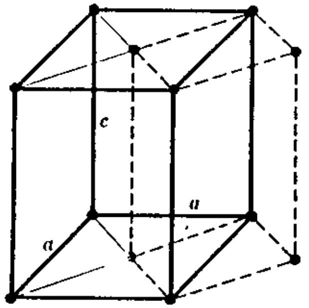


Fig. 2-4. Relation of tetragonal C lattice (full lines) to tetragonal P lattice (dashed lines).

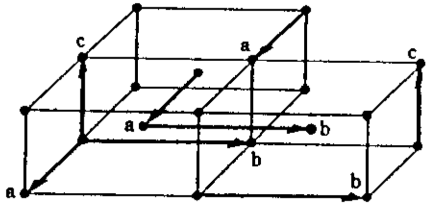
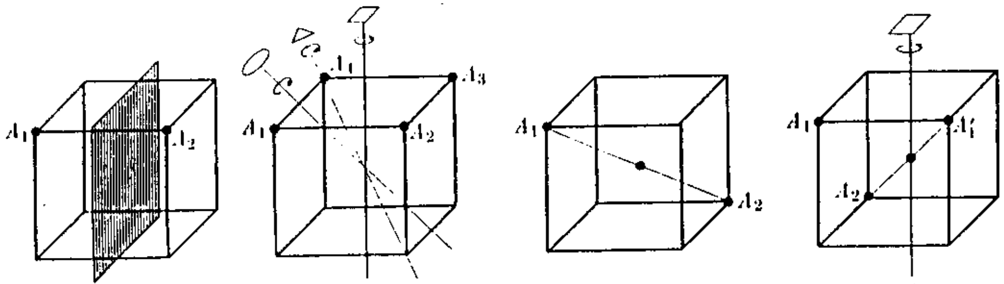


Fig. 2-5. Extension of lattice points through space by the unit cell vectors

The lattice points in a nonprimitive unit cell can be extended through space by repeated applications of the unit-cell vectors **a**, **b**, **c** just like those of a primitive cell. We may regard the lattice points associated with a unit cell as being translated one by one or as a group. In either case, equivalent lattice points in adjacent unit cells are separated by one of the vectors **a**, **b**, **c**, wherever these points happen to be located in the cell (Fig. 2–5).

2–4 Symmetry. Both Bravais lattices and the real crystals which are built up on them exhibit various kinds of symmetry. A body or structure is said to be symmetrical when its component parts are arranged in such balance, so to speak, that certain operations can be performed on the body which will bring it into coincidence with itself. These are termed *symmetry operations.* For example, if a body is symmetrical with respect to a plane passing through it, then reflection of either half of the body in the plane as in a mirror will produce a body coinciding with the other half. Thus a cube has several planes of symmetry, one of which is shown in Fig. 2–6(a).

There are in all four macroscopic* symmetry operations or elements: *reflection, rotation, inversion, and rotation-inversion.* A body has n-fold rotational symmetry about an axis if a rotation of 360°/n brings it into self-coincidence. Thus a cube has a 4-fold rotation axis normal to each face, a 3-fold axis along each body diagonal, and 2-fold axes joining the centers of opposite edges. Some of these are shown in Fig. 2–6(b) where the small plane figures (square, triangle, and ellipse) designate the various kinds of axes. In general, rotation axes may be 1-, 2-, 3-, 4-, or 6-fold. A 1-fold axis indicates no symmetry at all, while a 5-fold axis or one of higher degree than 6 is impossible, in the sense that unit cells having such symmetry cannot be made to fill up space without leaving gaps.



(a) (b) (c) (d)

FIG. 2–6. Some symmetry elements of a cube. (a) Reflection plane. A_1 becomes A_2. (b) Rotation axes. 4-fold axis: A_1 becomes A_2; 3-fold axis: A_1 becomes A_3; 2-fold axis: A_1 becomes A_4. (c) Inversion center. A_1 becomes A_2. (d) Rotation-inversion axis. 4-fold axis: A_1 becomes A_1'; inversion center: A_1' becomes A_2.

A body has an inversion center if corresponding points of the body are located at equal distances from the center on a line drawn through the center. A body having an inversion center will come into coincidence with itself if every point in the body is inverted, or "reflected," in the inversion center. A cube has such a center at the intersection of its body diagonals [Fig. 2–6(c)]. Finally, a body may have a rotation-inversion axis, either 1-, 2-, 3-, 4-, or 6-fold. If it has an n-fold rotation-inversion axis, it can be brought into coincidence with itself by a rotation of 360°/n about the axis followed by inversion in a center lying on the axis. Figure 2–6(d) illustrates the operation of a 4-fold rotation-inversion axis on a cube.

Now, the possession of a certain minimum set of symmetry elements is a fundamental property of each crystal system, and one system is distinguished from another just as much by its symmetry elements as by the values of its axial lengths and angles. In fact, these are interdependent. The minimum number of symmetry elements possessed by each crystal system is listed in Table 2–2. Some crystals may possess more than the minimum symmetry elements required by the system to which they belong, but none may have less.

Symmetry operations apply not only to the unit cells shown in Fig. 2–3, considered merely as geometric shapes, but also to the point lattices associated with them. The latter condition rules out the possibility that the cubic system, for example, could include a base-centered point lattice, since such an array of points would not have the minimum set of symmetry elements required by the cubic system, namely four 3-fold rotation axes. Such a lattice would be classified in the tetragonal system, which has no 3-fold axes and in which accidental equality of the a and c axes is

TABLE 2–2

SYMMETRY ELEMENTS

System	Minimum symmetry elements
Cubic	Four 3-fold rotation axes
Tetragonal	One 4-fold rotation (or rotation-inversion) axis
Orthorhombic	Three perpendicular 2-fold rotation (or rotation-inversion) axes
Rhombohedral	One 3-fold rotation (or rotation-inversion) axis
Hexagonal	One 6-fold rotation (or rotation-inversion) axis
Monoclinic	One 2-fold rotation (or rotation-inversion) axis
Triclinic	None

---

* So called to distinguish them from certain microscopic symmetry operations with which we are not concerned here. The macroscopic elements can be deduced from the angles between the faces of a well-developed crystal, without any knowledge of the atom arrangement inside the crystal. The microscopic symmetry elements, on the other hand, depend entirely on atom arrangement, and their presence cannot be inferred from the external development of the crystal.

allowed; as mentioned before, however, this lattice is simple, not base-centered, tetragonal.

Crystals in the rhombohedral (trigonal) system can be referred to either a rhombohedral or a hexagonal lattice. Appendix 2 gives the relation between these two lattices and the transformation equations which allow the Miller indices of a plane (see Sec. 2-6) to be expressed in terms of either set of axes.

2-5 Primitive and nonprimitive cells. In any point lattice a unit cell may be chosen in an infinite number of ways and may contain one or more lattice points per cell. It is important to note that unit cells do not "exist" as such in a lattice: they are a mental construct and can accordingly be chosen at our convenience. The conventional cells shown in Fig. 2-3 are chosen simply for convenience and to conform to the symmetry elements of the lattice.

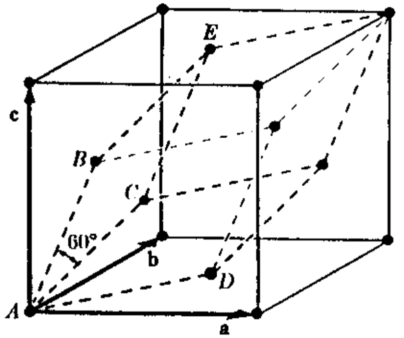


FIG. 2-7. Face-centered cubic point lattice referred to cubic and rhombohedral cells.

Any of the fourteen Bravais lattices may be referred to a primitive unit cell. For example, the face-centered cubic lattice shown in Fig. 2-7 may be referred to the primitive cell indicated by dashed lines. The latter cell is rhombohedral, its axial angle α is 60°, and each of its axes is $1/\sqrt{2}$ times the length of the axes of the cubic cell. Each cubic cell has four lattice points associated with it, each rhombohedral cell has one, and the former has, correspondingly, four times the volume of the latter. Nevertheless, it is usually more convenient to use the cubic cell rather than the rhombohedral one because the former immediately suggests the cubic symmetry which the lattice actually possesses. Similarly, the other centered nonprimitive cells listed in Table 2-1 are preferred to the primitive cells possible in their respective lattices.

If nonprimitive lattice cells are used, the vector from the origin to any point in the lattice will now have components which are nonintegral multiples of the unit-cell vectors **a**, **b**, **c**. The position of any lattice point in a cell may be given in terms of its *coordinates*; if the vector from the origin of the unit cell to the given point has components $x\mathbf{a}$, $y\mathbf{b}$, $z\mathbf{c}$, where x, y, and z are fractions, then the coordinates of the point are $x\ y\ z$. Thus, point A in Fig. 2-7, taken as the origin, has coordinates 0 0 0 while points B, C, and D, when referred to cubic axes, have coordinates $0\ \frac{1}{2}\ \frac{1}{2}$, $\frac{1}{2}\ 0\ \frac{1}{2}$, and $\frac{1}{2}\ \frac{1}{2}\ 0$, respectively. Point E has coordinates $\frac{1}{2}\ \frac{1}{2}\ 1$ and is equivalent to point D, being separated from it by the vector **c**. The coordinates of equivalent points in different unit cells can always be made identical by the addition or subtraction of a set of integral coordinates; in this case, subtraction of 0 0 1 from $\frac{1}{2}\ \frac{1}{2}\ 1$ (the coordinates of E) gives $\frac{1}{2}\ \frac{1}{2}\ 0$ (the coordinates of D).

Note that the coordinates of a body-centered point, for example, are always $\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$ no matter whether the unit cell is cubic, tetragonal, or orthorhombic, and whatever its size. The coordinates of a point position, such as $\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$, may also be regarded as an operator which, when "applied" to a point at the origin, will move or translate it to the position $\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$, the final position being obtained by simple addition of the operator $\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$ and the original position 0 0 0. In this sense, the positions 0 0 0, $\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$ are called the "body-centering translations," since they will produce the two point positions characteristic of a body-centered cell when applied to a point at the origin. Similarly, the four point positions characteristic of a face-centered cell, namely 0 0 0, $0\ \frac{1}{2}\ \frac{1}{2}$, $\frac{1}{2}\ 0\ \frac{1}{2}$, and $\frac{1}{2}\ \frac{1}{2}\ 0$, are called the face-centering translations. The base-centering translations depend on which pair of opposite faces are centered; if centered on the C face, for example, they are 0 0 0, $\frac{1}{2}\ \frac{1}{2}\ 0$.

2-6 Lattice directions and planes. The direction of any line in a lattice may be described by first drawing a line through the origin parallel to the given line and then giving the coordinates of any point on the line through the origin. Let the line pass through the origin of the unit cell and any point having coordinates $u\ v\ w$, where these numbers are not necessarily integral. (This line will also pass through the points $2u\ 2v\ 2w$, $3u\ 3v\ 3w$, etc.) Then $[uvw]$, written in square brackets, are the *indices* of the direction of the line. They are also the indices of any line parallel to the given line, since the lattice is infinite and the origin may be taken at any point. Whatever the values of u, v, w, they are always converted to a set of smallest integers by multiplication or division throughout: thus, $[\frac{1}{2}\ \frac{1}{2}\ 1]$, [112], and [224] all represent the same direction, but [112] is the preferred form. Negative indices are written with a bar over the number, e.g., $[\bar{u}vw]$. Direction indices are illustrated in Fig. 2-8.

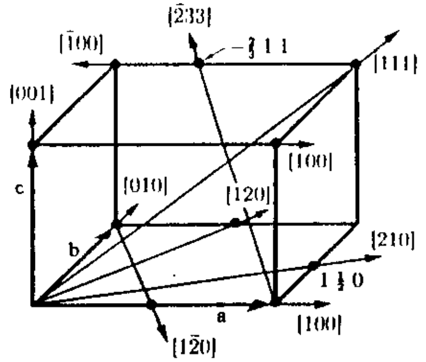
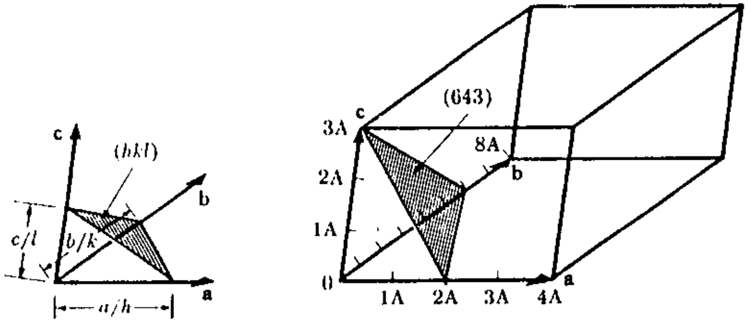


FIG. 2-8. Indices of directions.

Directions related by symmetry are called *directions of a form*, and a set of these are represented by the indices of one of them enclosed in angular brackets; for example, the four body diagonals of a cube, [111], [1$\bar{1}$1], [$\bar{1}\bar{1}$1], and [$\bar{1}$11], may all be represented by the symbol ⟨111⟩.

The orientation of planes in a lattice may also be represented symbolically, according to a system popularized by the English crystallographer Miller. In the general case, the given plane will be tilted with respect to the crystallographic axes, and, since these axes form a convenient frame of reference, we might describe the orientation of the plane by giving the actual distances, measured from the origin, at which it intercepts the three axes. Better still, by expressing these distances as fractions of the axial lengths, we can obtain numbers which are independent of the particular axial lengths involved in the given lattice. But a difficulty then arises when the given plane is parallel to a certain crystallographic axis, because such a plane does not intercept that axis, i.e., its "intercept" can only be described as "infinity." To avoid the introduction of infinity into the description of plane orientation, we can use the reciprocal of the fractional intercept, this reciprocal being zero when the plane and axis are parallel. We thus arrive at a workable symbolism for the orientation of a plane in a lattice, the *Miller indices*, which are defined as *the reciprocals of the fractional intercepts which the plane makes with the crystallographic axes.* For example, if the Miller indices of a plane are (hkl), written in parentheses, then the plane makes fractional intercepts of $1/h$, $1/k$, $1/l$ with the axes, and, if the axial lengths are a, b, c, the plane makes actual intercepts of a/h, b/k, c/l, as shown in Fig. 2-9(a). Parallel to any plane in any lattice, there is a whole set of parallel equidistant planes, one of which passes through the origin; the Miller indices (hkl) usually refer to that plane in the set which is nearest the origin, although they may be taken as referring to any other plane in the set or to the whole set taken together.

We may determine the Miller indices of the plane shown in Fig. 2-9(b) as follows:



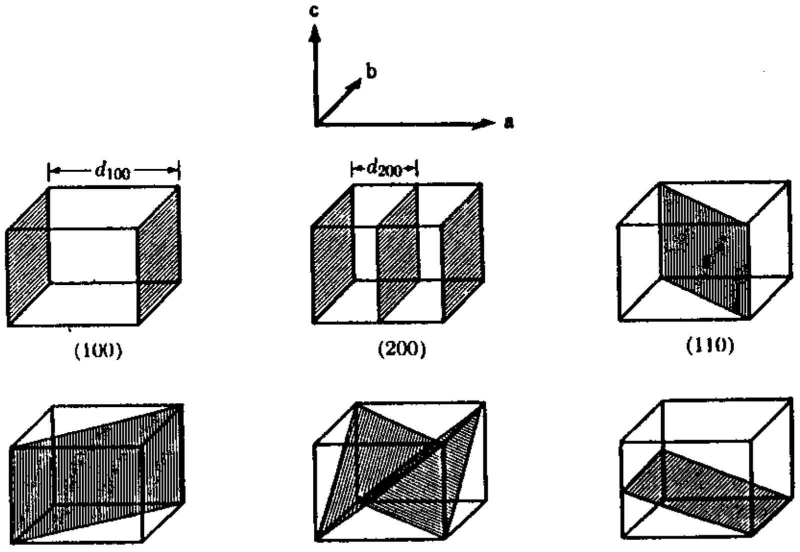
(a) (b)

FIG. 2-9. Plane designation by Miller indices.

Axial lengths	4A	8A	3A
Intercept lengths	2A	6A	3A
Fractional intercepts	$\frac{1}{2}$	$\frac{3}{4}$	1
Miller indices	2	$\frac{4}{3}$	1
	6	4	3

Miller indices are always cleared of fractions, as shown above. As stated earlier, if a plane is parallel to a given axis, its fractional intercept on that axis is taken as infinity and the corresponding Miller index is zero. If a plane cuts a negative axis, the corresponding index is negative and is written with a bar over it. Planes whose indices are the negatives of one another are parallel and lie on opposite sides of the origin, e.g., ($\bar{2}$10) and (2$\bar{1}$0). The planes ($nh\ nk\ nl$) are parallel to the planes (hkl) and have $1/n$ the spacing. The same plane may belong to two different sets, the Miller indices of one set being multiples of those of the other; thus the same plane belongs to the (210) set and the (420) set, and, in fact, the planes of the (210) set form every second plane in the (420) set. In the cubic system, it is convenient to remember that a direction [hkl] is always perpendicular to a plane (hkl) of the same indices, but this is not generally true in other systems. Further familiarity with Miller indices can be gained from a study of Fig. 2-10.

A slightly different system of plane indexing is used in the hexagonal system. The unit cell of a hexagonal lattice is defined by two equal and coplanar vectors $\mathbf{a}_1$ and $\mathbf{a}_2$, at 120° to one another, and a third axis $\mathbf{c}$ at right angles [Fig. 2-11(a)]. The complete lattice is built up, as usual, by



(100) (200) (110)

($\bar{1}$10) (11$\bar{1}$) (102)

FIG. 2-10. Miller indices of lattice planes.

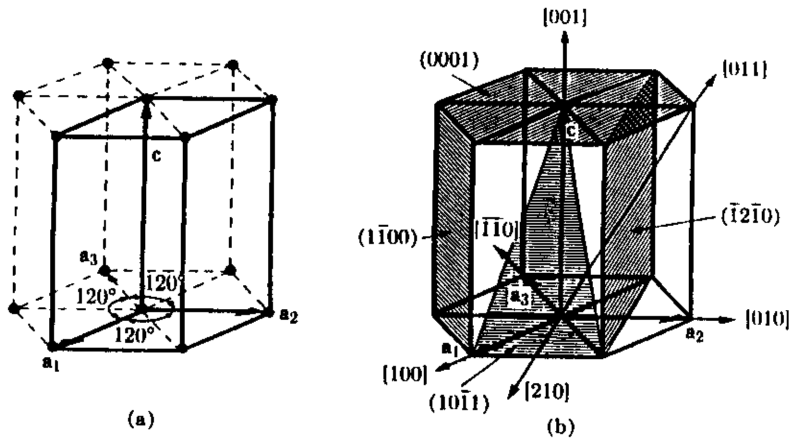


FIG. 2–11. (a) The hexagonal unit cell and (b) indices of planes and directions.

repeated translations of the points at the unit cell corners by the vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{c}$. Some of the points so generated are shown in the figure, at the ends of dashed lines, in order to exhibit the hexagonal symmetry of the lattice, which has a 6-fold rotation axis parallel to $\mathbf{c}$. The third axis $\mathbf{a}_3$, lying in the basal plane of the hexagonal prism, is so symmetrically related to $\mathbf{a}_1$ and $\mathbf{a}_2$ that it is often used in conjunction with the other two. Thus the indices of a plane in the hexagonal system, called Miller-Bravais indices, refer to *four* axes and are written $(hkil)$. The index i is the reciprocal of the fractional intercept on the $\mathbf{a}_3$ axis. Since the intercepts of a plane on $\mathbf{a}_1$ and $\mathbf{a}_2$ determine its intercept on $\mathbf{a}_3$, the value of i depends on the values of h and k. The relation is

$$h + k = -i. \tag{2-2}$$

Since i is determined by h and k, it is sometimes replaced by a dot and the plane symbol written $(hk \cdot l)$. However, this usage defeats the purpose for which Miller-Bravais indices were devised, namely, to give similar indices to similar planes. For example, the side planes of the hexagonal prism in Fig. 2–11(b) are all similar and symmetrically located, and their relationship is clearly shown in their full Miller-Bravais symbols: $(10\bar{1}0)$, $(01\bar{1}0)$, $(\bar{1}100)$, $(\bar{1}010)$, $(0\bar{1}10)$, $(1\bar{1}00)$. On the other hand, the abbreviated symbols of these planes, $(10 \cdot 0)$, $(01 \cdot 0)$, $(\bar{1}1 \cdot 0)$, $(\bar{1}0 \cdot 0)$, $(0\bar{1} \cdot 0)$, $(1\bar{1} \cdot 0)$ do not immediately suggest this relationship.

Directions in a hexagonal lattice are best expressed in terms of the *three* basic vectors $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{c}$. Figure 2–11(b) shows several examples of both plane and direction indices. (Another system, involving four indices, is sometimes used to designate directions. The required direction is broken up into four component vectors, parallel to $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$, and $\mathbf{c}$ and so chosen that the third index is the negative of the sum of the first two.

[100], for example, becomes $[2\bar{1}\bar{1}0]$, [210] becomes $[10\bar{1}0]$, [010] becomes $[\bar{1}2\bar{1}0]$, etc.)

In any crystal system there are sets of equivalent lattice planes related by symmetry. These are called *planes of a form*, and the indices of any one plane, enclosed in braces $\{hkl\}$, stand for the whole set. In general, planes of a form have the same spacing but different Miller indices. For example, the faces of a cube, (100), (010), $(\bar{1}00)$, $(0\bar{1}0)$, (001), and $(00\bar{1})$, are planes of the form $\{100\}$, since all of them may be generated from any one by operation of the 4-fold rotation axes perpendicular to the cube faces. In the tetragonal system, however, only the planes (100), (010), $(\bar{1}00)$, and $(0\bar{1}0)$ belong to the form $\{100\}$; the other two planes, (001) and $(00\bar{1})$, belong to the different form $\{001\}$; the first four planes mentioned are related by a 4-fold axis and the last two by a 2-fold axis.*

Planes of a zone are planes which are all parallel to one line, called the *zone axis*, and the zone, i.e., the set of planes, is specified by giving the indices of the zone axis. Such planes may have quite different indices and spacings, the only requirement being their parallelism to a line. Figure 2–12 shows some examples. If the axis of a zone has indices $[uvw]$, then any plane belongs to that zone whose indices (hkl) satisfy the relation

$$hu + kv + lw = 0. \tag{2-3}$$

(A proof of this relation is given in Section 3 of Appendix 15.) Any two nonparallel planes are planes of a zone since they are both parallel to their line of intersection. If their indices are $(h_1k_1l_1)$ and $(h_2k_2l_2)$, then the indices of their zone axis $[uvw]$ are given by the relations

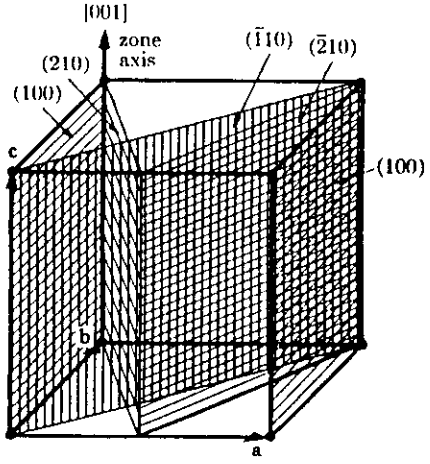


FIG. 2–12. All shaded planes in the cubic lattice shown are planes of the zone [001].

$$\begin{aligned} u &= k_1l_2 - k_2l_1, \\ v &= l_1h_2 - l_2h_1, \\ w &= h_1k_2 - h_2k_1. \end{aligned} \tag{2-4}$$

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* Certain important crystal planes are often referred to by name without any mention of their Miller indices. Thus, planes of the form $\{111\}$ in the cubic system are often called octahedral planes, since these are the bounding planes of an octahedron. In the hexagonal system, the (0001) plane is called the basal plane, planes of the form $\{10\bar{1}0\}$ are called prismatic planes, and planes of the form $\{10\bar{1}1\}$ are called pyramidal planes.

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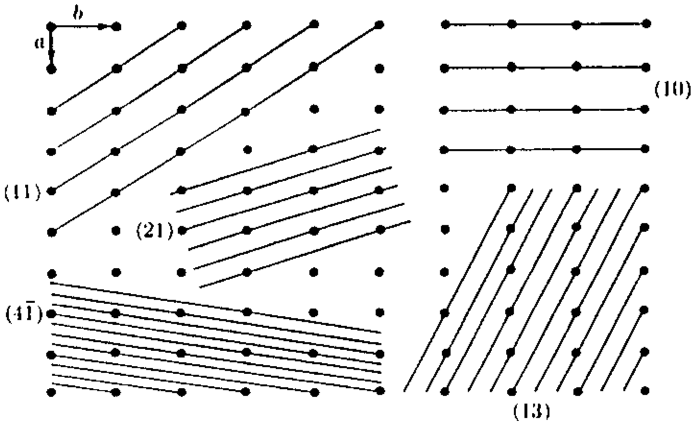

FIG. 2-13. Two-dimensional lattice, showing that lines of lowest indices have the greatest spacing and the greatest density of lattice points.

The various sets of planes in a lattice have various values of interplanar spacing. The planes of large spacing have low indices and pass through a high density of lattice points, whereas the reverse is true of planes of small spacing. Figure 2-13 illustrates this for a two-dimensional lattice, and it is equally true in three dimensions. The interplanar spacing d_{hkl}, measured at right angles to the planes, is a function both of the plane indices (hkl) and the lattice constants $(a, b, c, \alpha, \beta, \gamma)$. The exact relation depends on the crystal system involved and for the cubic system takes on the relatively simple form

$$\text{(Cubic)} \quad d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}. \tag{2-5}$$

In the tetragonal system the spacing equation naturally involves both a and c since these are not generally equal:

$$\text{(Tetragonal)} \quad d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2\,(a^2/c^2)}}. \tag{2-6}$$

Interplanar spacing equations for all systems are given in Appendix 1.

2-7 Crystal structure. So far we have discussed topics from the field of *mathematical (geometrical) crystallography* and have said practically nothing about actual crystals and the atoms of which they are composed. In fact, all of the above was well known long before the discovery of x-ray diffraction, i.e., long before there was any certain knowledge of the interior arrangements of atoms in crystals.

It is now time to describe the structure of some actual crystals and to relate this structure to the point lattices, crystal systems, and symmetry elements discussed above. The cardinal principle of crystal structure is that *the atoms of a crystal are set in space either on the points of a Bravais lattice or in some fixed relation to those points.* It follows from this that the atoms of a crystal will be arranged periodically in three dimensions and that this arrangement of atoms will exhibit many of the properties of a Bravais lattice, in particular many of its symmetry elements.

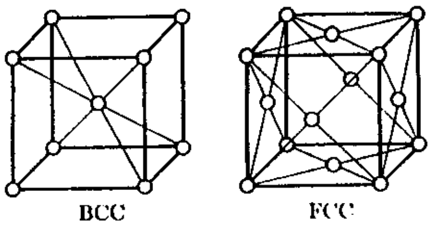

FIG. 2-14. Structures of some common metals. Body-centered cubic: α-Fe, Cr, Mo, V, etc.; face-centered cubic: γ-Fe, Cu, Pb, Ni, etc.

The simplest crystals one can imagine are those formed by placing atoms of the same kind *on* the points of a Bravais lattice. Not all such crystals exist but, fortunately for metallurgists, many metals crystallize in this simple fashion, and Fig. 2-14 shows two common structures based on the body-centered cubic (BCC) and face-centered cubic (FCC) lattices. The former has two atoms per unit cell and the latter four, as we can find by rewriting Eq. (2-1) in terms of the number of atoms, rather than lattice points, per cell and applying it to the unit cells shown.

The next degree of complexity is encountered when two or more atoms of the same kind are "associated with" each point of a Bravais lattice, as exemplified by the hexagonal close-packed (HCP) structure common to many metals. This structure is simple hexagonal and is illustrated in Fig. 2-15. There are two atoms per unit cell, as shown in (a), one at 0 0 0 and the other at $\frac{2}{3}\,\frac{1}{3}\,\frac{1}{2}$ (or at $\frac{1}{3}\,\frac{2}{3}\,\frac{1}{2}$, which is an equivalent position). Figure 2-15(b) shows the same structure with the origin of the unit cell shifted so that the point 1 0 0 in the new cell is midway between the atoms at 1 0 0 and $\frac{2}{3}\,\frac{1}{3}\,\frac{1}{2}$ in (a), the nine atoms shown in (a) corresponding to the nine atoms marked with an X in (b). The "association" of pairs of atoms with the points of a simple hexagonal Bravais lattice is suggested by the dashed lines in (b). Note, however, that the atoms of a close-packed hexagonal structure do not themselves form a point lattice, the surroundings of an atom at 0 0 0 being different from those of an atom at $\frac{2}{3}\,\frac{1}{3}\,\frac{1}{2}$. Figure 2-15(c) shows still another representation of the HCP structure: the three atoms in the interior of the hexagonal prism are directly above the centers of alternate triangles in the base and, if repeated through space by the vectors $\mathbf{a}_1$ and $\mathbf{a}_2$, would also form a hexagonal array just like the atoms in the layers above and below.

The HCP structure is so called because it is one of the two ways in which spheres can be packed together in space with the greatest possible density and still have a periodic arrangement. Such an arrangement of spheres in contact is shown in Fig. 2-15(d). If these spheres are regarded

CHAPTER 3

DIFFRACTION I: THE DIRECTIONS OF DIFFRACTED BEAMS

3-1 Introduction. After our preliminary survey of the physics of x-rays and the geometry of crystals, we can now proceed to fit the two together and discuss the phenomenon of x-ray diffraction, which is an interaction of the two. Historically, this is exactly the way this field of science developed. For many years, mineralogists and crystallographers had accumulated knowledge about crystals, chiefly by measurement of interfacial angles, chemical analysis, and determination of physical properties. There was little knowledge of interior structure, however, although some very shrewd guesses had been made, namely, that crystals were built up by periodic repetition of some unit, probably an atom or molecule, and that these units were situated some 1 or 2A apart. On the other hand, there were indications, but only indications, that x-rays might be electromagnetic waves about 1 or 2A in wavelength. In addition, the phenomenon of diffraction was well understood, and it was known that diffraction, as of visible light by a ruled grating, occurred whenever wave motion encountered a set of regularly spaced scattering objects, provided that the wavelength of the wave motion was of the same order of magnitude as the repeat distance between the scattering centers.

Such was the state of knowledge in 1912 when the German physicist von Laue took up the problem. He reasoned that, *if* crystals were composed of regularly spaced atoms which might act as scattering centers for x-rays, and *if* x-rays were electromagnetic waves of wavelength about equal to the interatomic distance in crystals, then it should be possible to diffract x-rays by means of crystals. Under his direction, experiments to test this hypothesis were carried out: a crystal of copper sulfate was set up in the path of a narrow beam of x-rays and a photographic plate was arranged to record the presence of diffracted beams, if any. The very first experiment was successful and showed without doubt that x-rays *were* diffracted by the crystal out of the primary beam to form a pattern of spots on the photographic plate. These experiments proved, at one and the same time, the wave nature of x-rays and the periodicity of the arrangement of atoms within a crystal. Hindsight is always easy and these ideas appear quite simple to us now, when viewed from the vantage point of more than forty years' development of the subject, but they were not at all obvious in 1912, and von Laue's hypothesis and its experimental verification must stand as a great intellectual achievement.

The account of these experiments was read with great interest by two English physicists, W. H. Bragg and his son W. L. Bragg. The latter, although only a young student at the time—it was still the year 1912—successfully analyzed the Laue experiment and was able to express the necessary conditions for diffraction in a somewhat simpler mathematical form than that used by von Laue. He also attacked the problem of crystal structure with the new tool of x-ray diffraction and, in the following year, solved the structures of NaCl, KCl, KBr, and KI, all of which have the NaCl structure; these were the first complete crystal-structure determinations ever made.

3-2 Diffraction. Diffraction is due essentially to the existence of certain phase relations between two or more waves, and it is advisable, at the start, to get a clear notion of what is meant by phase relations. Consider a beam of x-rays, such as beam **1** in Fig. 3-1, proceeding from left to right. For convenience only, this beam is assumed to be plane-polarized in order that we may draw the electric field vector **E** always in one plane. We may imagine this beam to be composed of two equal parts, ray **2** and ray **3**, each of half the amplitude of beam **1**. These two rays, on the wave front AA', are said to be completely *in phase* or in step; i.e., their electric-field vectors have the same magnitude and direction at the same instant at any point x measured along the direction of propagation of the wave. A *wave front* is a surface perpendicular to this direction of propagation.

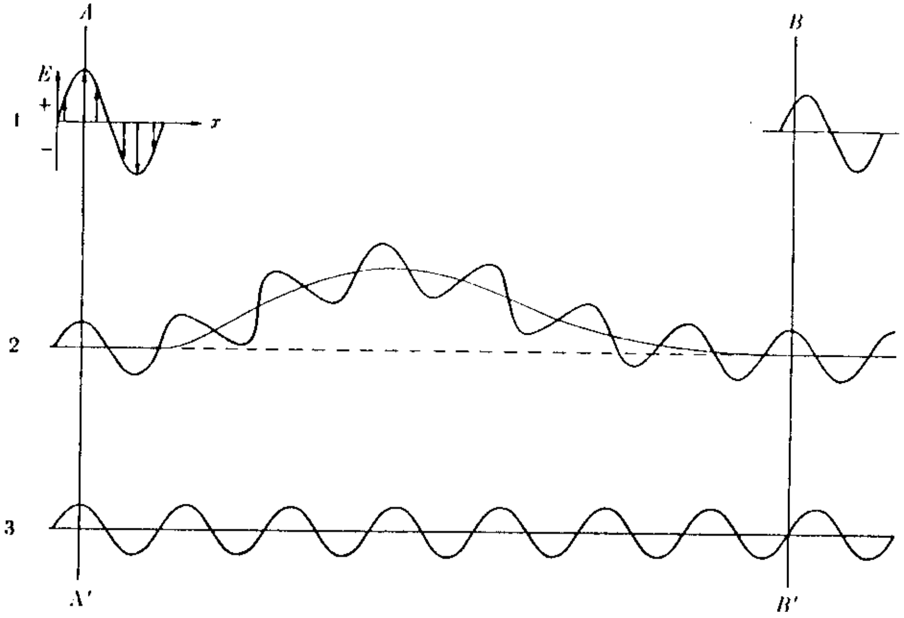

FIG. 3-1. Effect of path difference on relative phase.

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

Two conclusions may be drawn from this illustration:

(1) Differences in the length of the path traveled lead to differences in phase.

(2) The introduction of phase differences produces a change in amplitude.

The greater the path difference, the greater the difference in phase, since the path difference, measured in wavelengths, exactly equals the phase difference, also measured in wavelengths. If the diverted path of ray **2** in Fig. 3-1 were a quarter wavelength longer than shown, the phase difference would be a half wavelength. The two rays would then be completely out of phase on the wave front BB' and beyond, and they would therefore annul each other, since at any point their electric vectors would be either both zero or of the same magnitude and opposite in direction. If the difference in path length were made three quarters of a wavelength greater than shown, the two rays would be one complete wavelength out of phase, a condition indistinguishable from being completely in phase since in both cases the two waves would combine to form a beam of amplitude 2 units, just like the original beam. We may conclude that two rays are completely in phase whenever their path lengths differ either by zero or by a whole number of wavelengths.

Differences in the path length of various rays arise quite naturally when we consider how a crystal diffracts x-rays. Figure 3-2 shows a section of a crystal, its atoms arranged on a set of parallel planes A, B, C, D, $\ldots$, normal to the plane of the drawing and spaced a distance d' apart. Assume that a beam of perfectly parallel, perfectly monochromatic x-rays of wavelength λ is incident on this crystal at an angle θ, called the Bragg angle, where θ is measured between the incident beam and the particular crystal planes under consideration.

We wish to know whether this incident beam of x-rays will be diffracted by the crystal and, if so, under what conditions. *A diffracted beam may be defined as a beam composed of a large number of scattered rays mutually reinforcing one another.* Diffraction is, therefore, essentially a scattering phenomenon and not one involving any "new" kind of interaction between x-rays and atoms. We saw in Sec. 1-5 that atoms scatter incident x-rays in all directions, and we shall see presently that in some of these directions the scattered beams will be completely in phase and so reinforce each other to form diffracted beams.

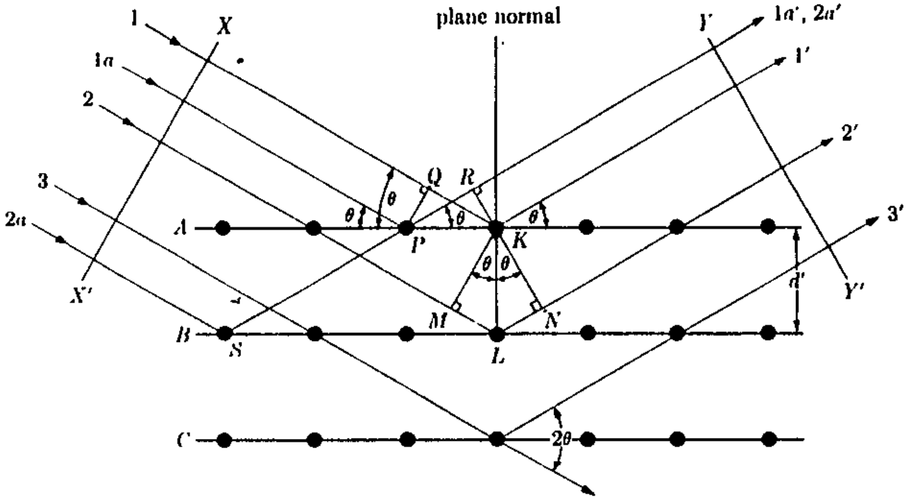

FIG. 3-2. Diffraction of x-rays by a crystal.

For the particular conditions described by Fig. 3-2 the only diffracted beam formed is that shown, namely one making an angle θ of reflection[*] equal to the angle θ of incidence. We will show this, first, for one plane of atoms and, second, for all the atoms making up the crystal. Consider rays 1 and **1a** in the incident beam; they strike atoms K and P in the first plane of atoms and are scattered in all directions. Only in the directions **1'** and **1a'**, however, are these scattered beams completely in phase and so capable of reinforcing one another; they do so because the difference in their length of path between the wave fronts XX' and YY' is equal to

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

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

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

the path difference for rays **1***K***1′** and **2***L***2′** is

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

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

$$n\lambda = 2d' \sin \theta. \tag{3-1}$$

This relation was first formulated by W. L. Bragg and is known as the Bragg law. It states the essential condition which must be met if diffraction is to occur. n is called the order of reflection; it may take on any integral value consistent with $\sin \theta$ not exceeding unity and is equal to the number of wavelengths in the path difference between rays scattered by *adjacent* planes. Therefore, for fixed values of λ and d', there may be several angles of incidence θ_1, θ_2, θ_3 ... at which diffraction may occur, corresponding to $n = 1, 2, 3, \ldots$. In a first-order reflection ($n = 1$), the scattered rays **1′** and **2′** of Fig. 3–2 would differ in length of path (and in phase) by one wavelength, rays **1′** and **3′** by two wavelengths, rays **1′** and **4′** by three wavelengths, and so on throughout the crystal. The rays scattered by all the atoms in all the planes are therefore completely in phase and reinforce one another (constructive interference) to form a diffracted beam in the direction shown. In all other directions of space the scattered beams are out of phase and annul one another (destructive interference). The diffracted beam is rather strong compared to the sum of all the rays scattered in the same direction, simply because of the reinforcement which occurs,* but extremely weak compared to the incident beam since the atoms of a crystal scatter only a small fraction of the energy incident on them.

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

We have here regarded a diffracted beam as being built up of rays scattered by successive planes of atoms within the crystal. It would be a mistake to assume, however, that a single plane of atoms A would diffract x-rays just as the complete crystal does but less strongly. Actually, the single plane of atoms would produce, not only the beam in the direction **1′** as the complete crystal does, but also additional beams in other directions, some of them not confined to the plane of the drawing. These additional beams do not exist in the diffraction from the complete crystal precisely because the atoms in the other planes scatter beams which destructively interfere with those scattered by the atoms in plane A, *except* in the direction **1′**.

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

(1) The diffracted beam from a crystal is built up of rays scattered by all the atoms of the crystal which lie in the path of the incident beam. The reflection of visible light takes place in a thin surface layer only.

(2) The diffraction of monochromatic x-rays takes place only at those particular angles of incidence which satisfy the Bragg law. The reflection of visible light takes place at any angle of incidence.

(3) The reflection of visible light by a good mirror is almost 100 percent efficient. The intensity of a diffracted x-ray beam is extremely small compared to that of the incident beam.

Despite these differences, we often speak of "reflecting planes" and "reflected beams" when we really mean diffracting planes and diffracted beams. This is common usage and, from now on, we will frequently use these terms without quotation marks but with the tacit understanding that we really mean diffraction and not reflection.*

To sum up, diffraction is essentially a scattering phenomenon in which a large number of atoms cooperate. Since the atoms are arranged periodically on a lattice, the rays scattered by them have definite phase relations between them; these phase relations are such that destructive interference occurs in most directions of scattering, but in a few directions constructive interference takes place and diffracted beams are formed. The two essentials are a wave motion capable of interference (x-rays) and a set of periodically arranged scattering centers (the atoms of a crystal).

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* For the sake of completeness, it should be mentioned that x-rays *can* be totally reflected by a solid surface, just like visible light by a mirror, but only at very small angles of incidence (below about one degree). This phenomenon is of little practical importance in x-ray metallography and need not concern us further.

3-3 The Bragg law. Two geometrical facts are worth remembering:

(1) The incident beam, the normal to the reflecting plane, and the diffracted beam are always coplanar.

(2) The angle between the diffracted beam and the transmitted beam is always 2θ. This is known as the diffraction angle, and it is this angle, rather than θ, which is usually measured experimentally.

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

$$\frac{n\lambda}{2d'} = \sin\theta < 1. \qquad (3\text{-}2)$$

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

$$\lambda < 2d'. \qquad (3\text{-}3)$$

For most sets of crystal planes d' is of the order of 3A or less, which means that λ cannot exceed about 6A. A crystal could not possibly diffract ultraviolet radiation, for example, of wavelength about 500A. On the other hand, if λ is very small, the diffraction angles are too small to be conveniently measured.

The Bragg law may be written in the form

$$\lambda = 2\frac{d'}{n}\sin\theta. \qquad (3\text{-}4)$$

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

$$\boxed{\lambda = 2d\sin\theta}. \qquad (3\text{-}5)$$

This form will be used throughout this book.

This usage is illustrated by Fig. 3-3. Consider the second-order 100 reflection* shown in (a). Since it is second-order, the path difference ABC between rays scattered by adjacent (100) planes must be two whole wavelengths. If there is no real plane of atoms between the (100) planes, we can always imagine one as in Fig. 3-3(b), where the dotted plane midway between the (100) planes forms part of the (200) set of planes. For the same reflection as in (a), the path difference DEF between rays scattered by adjacent (200) planes is now only one whole wavelength, so that this reflection can properly be called a first-order 200 reflection. Similarly, 300, 400, etc., reflections are equivalent to reflections of the third, fourth, etc., orders from the (100) planes. In general, an nth-order reflection from (hkl) planes of spacing d' may be considered as a first-order reflection from the $(nh\ nk\ nl)$ planes of spacing $d = d'/n$. Note that this convention is in accord with the definition of Miller indices since $(nh\ nk\ nl)$ are the Miller indices of planes parallel to the (hkl) planes but with $1/n$ the spacing of the latter.

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* This means the reflection from the (100) planes. Conventionally, the Miller indices of a reflecting plane hkl, written without parentheses, stand for the reflected beam from the plane (hkl).

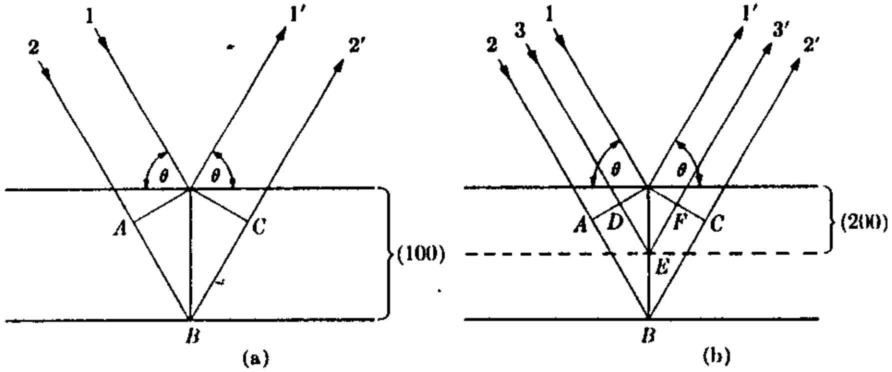

FIG. 3-3. Equivalence of (a) a second-order 100 reflection and (b) a first-order 200 reflection.

3-4 X-ray spectroscopy. Experimentally, the Bragg law can be utilized in two ways. By using x-rays of known wavelength λ and measuring θ, we can determine the spacing d of various planes in a crystal: this is *structure analysis* and is the subject, in one way or another, of the greater part of this book. Alternatively, we can use a crystal with planes of known spacing d, measure θ, and thus determine the wavelength λ of the radiation used: this is *x-ray spectroscopy*.

The essential features of an x-ray spectrometer are shown in Fig. 3-4. X-rays from the tube T are incident on a crystal C which may be set at any desired angle to the incident

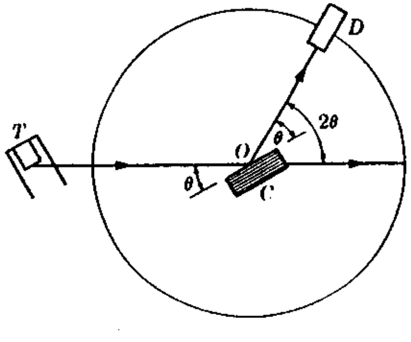

FIG. 3-4. The x-ray spectrometer.

APPENDIX 15

THE RECIPROCAL LATTICE

A15–1 Introduction. All the diffraction phenomena described in this book have been discussed in terms of the Bragg law. This simple law, admirable for its very simplicity, is in fact applicable to a very wide range of phenomena and is all that is needed for an understanding of a great many applications of x-ray diffraction. Yet there are diffraction effects which the Bragg law is totally unable to explain, notably those involving diffuse scattering at non-Bragg angles, and these effects demand a more general theory of diffraction for their explanation. The reciprocal lattice provides the framework for such a theory. This powerful concept was introduced into the field of diffraction by the German physicist Ewald in 1921 and has since become an indispensable tool in the solution of many problems.

Although the reciprocal lattice may at first appear rather abstract or artificial, the time spent in grasping its essential features is time well spent, because the reciprocal-lattice theory of diffraction, being general, is applicable to all diffraction phenomena from the simplest to the most intricate. Familiarity with the reciprocal lattice will therefore not only provide the student with the necessary key to complex diffraction effects but will deepen his understanding of even the simplest.

A15–2 Vector multiplication. Since the reciprocal lattice is best formulated in terms of vectors, we shall first review a few theorems of vector algebra, namely, those involving the multiplication of vector quantities.

The *scalar product* (or dot product) of two vectors* $\mathbf{a}$ and $\mathbf{b}$, written $\mathbf{a}\cdot\mathbf{b}$, is a scalar quantity equal in magnitude to the product of the absolute values of the two vectors and the cosine of the angle α between them, or

$$\mathbf{a}\cdot\mathbf{b} = ab\cos\alpha.$$

Geometrically, Fig. A15–1 shows that the scalar product of two vectors may be regarded as the product of the length of one vector and the projection of the other upon the first. If one of the vectors, say $\mathbf{a}$, is a unit vector (a vector of unit length), then $\mathbf{a}\cdot\mathbf{b}$ gives immediately the length of the projection of $\mathbf{b}$ on $\mathbf{a}$. The scalar product of sums or differences of vectors is formed simply by term-by-term multiplication:

$$(\mathbf{a}+\mathbf{b})\cdot(\mathbf{c}-\mathbf{d}) = (\mathbf{a}\cdot\mathbf{c}) - (\mathbf{a}\cdot\mathbf{d}) + (\mathbf{b}\cdot\mathbf{c}) - (\mathbf{b}\cdot\mathbf{d}).$$

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* Bold-face symbols stand for vectors. The same symbol in italic stands for

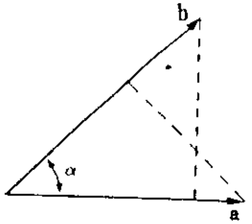


Fig. A15–1. Scalar product of two vectors.

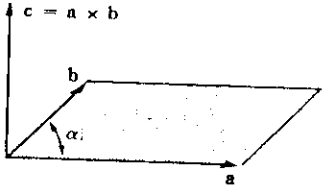


Fig. A15–2. Vector product of two vectors.

The order of multiplication is of no importance; i.e.,

$$\mathbf{a}\cdot\mathbf{b} = \mathbf{b}\cdot\mathbf{a}.$$

The *vector product* (or cross product) of two vectors $\mathbf{a}$ and $\mathbf{b}$, written $\mathbf{a}\times\mathbf{b}$, is *a vector* $\mathbf{c}$ at right angles to the plane of $\mathbf{a}$ and $\mathbf{b}$, and equal in magnitude to the product of the absolute values of the two vectors and the sine of the angle α between them, or

$$\mathbf{c} = \mathbf{a}\times\mathbf{b},$$

$$c = ab\sin\alpha.$$

The magnitude of $\mathbf{c}$ is simply the area of the parallelogram constructed on $\mathbf{a}$ and $\mathbf{b}$, as suggested by Fig. A15–2. The direction of $\mathbf{c}$ is that in which a right-hand screw would move if rotated in such a way as to bring $\mathbf{a}$ into $\mathbf{b}$. It follows from this that the direction of the vector product $\mathbf{c}$ is reversed if the order of multiplication is reversed, or that

$$\mathbf{a}\times\mathbf{b} = -(\mathbf{b}\times\mathbf{a}).$$

A15–3 The reciprocal lattice. Corresponding to any crystal lattice, we can construct a *reciprocal lattice*, so called because many of its properties are reciprocal to those of the crystal lattice. Let the crystal lattice have a unit cell defined by the vectors $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$. Then the corresponding reciprocal lattice has a unit cell defined by the vectors $\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$, where

$$\mathbf{b}_1 = \frac{1}{V}(\mathbf{a}_2\times\mathbf{a}_3), \qquad (1)$$

$$\mathbf{b}_2 = \frac{1}{V}(\mathbf{a}_3\times\mathbf{a}_1), \qquad (2)$$

$$\mathbf{b}_3 = \frac{1}{V}(\mathbf{a}_1\times\mathbf{a}_2), \qquad (3)$$

and V is the volume of the crystal unit cell. This way of defining the vectors $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$ in terms of the vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ gives the reciprocal lattice certain useful properties which we will now investigate

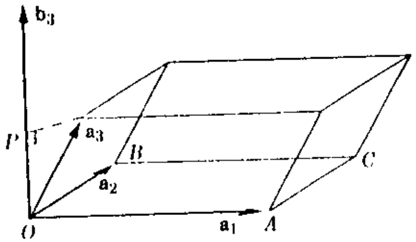


FIG. A15-3. Location of the reciprocal-lattice axis $\mathbf{b}_3$.

Consider the general triclinic unit cell shown in Fig. A15-3. The reciprocal-lattice axis $\mathbf{b}_3$ is, according to Eq. (3), normal to the plane of $\mathbf{a}_1$ and $\mathbf{a}_2$, as shown. Its length is given by

$$b_3 = \frac{|\mathbf{a}_1 \times \mathbf{a}_2|}{V}$$

$$= \frac{(\text{area of parallelogram } OACB)}{(\text{area of parallelogram } OACB)(\text{height of cell})}$$

$$= \frac{1}{OP} = \frac{1}{d_{001}},$$

since OP, the projection of $\mathbf{a}_3$ on $\mathbf{b}_3$, is equal to the height of the cell, which in turn is simply the spacing d of the (001) planes of the crystal lattice. Similarly, we find that the reciprocal lattice axes $\mathbf{b}_1$ and $\mathbf{b}_2$ are normal to the (100) and (010) planes, respectively, of the crystal lattice, and are equal in length to the reciprocals of the spacings of these planes.

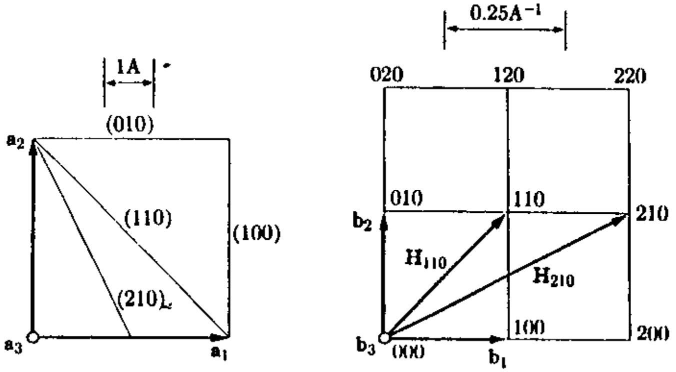
By extension, similar relations are found for all the planes of the crystal lattice. The whole reciprocal lattice is built up by repeated translations of the unit cell by the vectors $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$. This produces an array of points each of which is labeled with its coordinates in terms of the basic vectors. Thus, the point at the end of the $\mathbf{b}_1$ vector is labeled 100, that at the end of the $\mathbf{b}_2$ vector 010, etc. This extended reciprocal lattice has the following properties:

(1) A vector $\mathbf{H}_{hkl}$ drawn from the origin of the reciprocal lattice to any point in it having coordinates hkl is perpendicular to the plane in the crystal lattice whose Miller indices are hkl. This vector is given in terms of its coordinates by the expression

$$\mathbf{H}_{hkl} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3.$$

(2) The length of the vector $\mathbf{H}_{hkl}$ is equal to the reciprocal of the spacing d of the (hkl) planes, or

$$H_{hkl} = \frac{1}{d_{hkl}}.$$



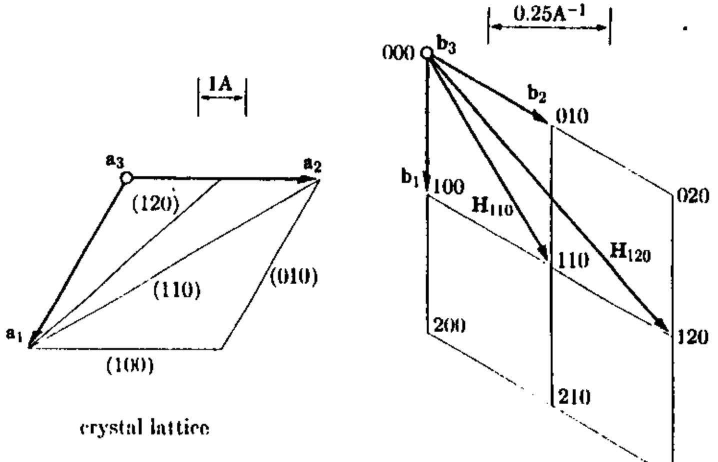
crystal lattice

reciprocal lattice

FIG. A15-4. The reciprocal lattice of a cubic crystal which has $a_1 = 4$A. The axes $\mathbf{a}_3$ and $\mathbf{b}_3$ are normal to the drawing.

The important thing to note about these relations is that the reciprocal-lattice array of points completely describes the crystal, in the sense that each reciprocal-lattice point is related to a set of planes in the crystal and represents the orientation and spacing of that set of planes.

Before proving these general relations, we might consider particular examples of the reciprocal lattice as shown in Figs. A15-4 and A15-5 for cubic and hexagonal crystals. In each case, the reciprocal lattice is drawn from any convenient origin, not necessarily that of the crystal lattice, and to any convenient scale of reciprocal angstroms. Note that Eqs. (1) through (3) take on a very simple form for any crystal whose unit cell is



crystal lattice

reciprocal lattice

FIG. A15-5. The reciprocal lattice of a hexagonal crystal which has $a_1 = 4$A. (Here the three-symbol system of plane indexing is used and $\mathbf{a}_3$ is the axis usually designated $\mathbf{c}$.) The axes $\mathbf{a}_3$ and $\mathbf{b}_3$ are normal to the drawing.

based on mutually perpendicular vectors, i.e., cubic, tetragonal, or orthorhombic. For such crystals, $\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$ are parallel, respectively, to $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$, while b_1, b_2, and b_3 are simply the reciprocals of a_1, a_2, and a_3. In Figs. A15–4 and A15–5, four cells of the reciprocal lattice are shown, together with two **H** vectors in each case. By means of the scales shown, it may be verified that each **H** vector is equal in length to the reciprocal of the spacing of the corresponding planes and normal to them. Note that reciprocal lattice points such as *nh*, *nk*, *nl*, where *n* is an integer, correspond to planes parallel to (*hkl*) and having $1/n$ their spacing. Thus, $\mathbf{H}_{220}$ is perpendicular to (220) planes and therefore parallel to $\mathbf{H}_{110}$, since (110) and (220) are parallel, but $\mathbf{H}_{220}$ is twice as long as $\mathbf{H}_{110}$ since the (220) planes have half the spacing of the (110) planes.

Other useful relations between the crystal and reciprocal vectors follow from Eqs. (1) through (3). Since $\mathbf{b}_3$, for example, is normal to both $\mathbf{a}_1$ and $\mathbf{a}_2$, its dot product with either one of these vectors is zero, or

$$\mathbf{b}_3 \cdot \mathbf{a}_1 = \mathbf{b}_3 \cdot \mathbf{a}_2 = 0.$$

The dot product of $\mathbf{b}_3$ and $\mathbf{a}_3$, however, is unity, since (see Fig. A15–3)

$$\begin{aligned} \mathbf{b}_3 \cdot \mathbf{a}_3 &= (b_3)\ (\text{projection of } \mathbf{a}_3 \text{ on } \mathbf{b}_3) \\ &= \left(\frac{1}{OP}\right)(OP) \\ &= 1. \end{aligned}$$

In general,

$$\begin{aligned} \mathbf{a}_m \cdot \mathbf{b}_n &= 1, \quad \text{if } m = n, && (4) \\ &= 0, \quad \text{if } m \neq n. && (5) \end{aligned}$$

The fact that $\mathbf{H}_{hkl}$ is normal to (*hkl*) and H_{hkl} is the reciprocal of d_{hkl} may be proved as follows. Let *ABC* of Fig. A15–6 be part of the plane nearest the origin in the set (*hkl*). Then, from the definition of Miller indices, the vectors from the origin to the points *A*, *B*, and *C* are $\mathbf{a}_1/h$, $\mathbf{a}_2/k$, and $\mathbf{a}_3/l$, respectively. Consider the vector **AB**, that is, a vector drawn from *A* to *B*, lying in the plane (*hkl*). Since

$$\frac{\mathbf{a}_1}{h} + \mathbf{AB} = \frac{\mathbf{a}_2}{k},$$

then

$$\mathbf{AB} = \frac{\mathbf{a}_2}{k} - \frac{\mathbf{a}_1}{h}.$$

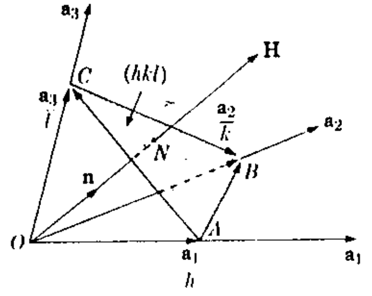


Fig. A15–6. Relation between reciprocal-lattice vector **H** and crystal plane (*hkl*).

Forming the dot product of **H** and **AB**, we have

$$\mathbf{H} \cdot \mathbf{AB} = (h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3) \cdot \left(\frac{\mathbf{a}_2}{k} - \frac{\mathbf{a}_1}{h}\right).$$

Evaluating this with the aid of Eqs. (4) and (5), we find

$$\mathbf{H} \cdot \mathbf{AB} = 1 - 1 = 0.$$

Since this product is zero, **H** must be normal to **AB**. Similarly, it may be shown that **H** is normal to **AC**. Since **H** is normal to two vectors in the plane (*hkl*), it is normal to the plane itself.

To prove the reciprocal relation between *H* and *d*, let **n** be a unit vector in the direction of **H**, i.e., normal to (*hkl*). Then

$$d = ON = \frac{\mathbf{a}_1}{h} \cdot \mathbf{n}.$$

But

$$\mathbf{n} = \frac{\mathbf{H}}{H}.$$

Therefore

$$\begin{aligned} d &= \frac{\mathbf{a}_1}{h} \cdot \frac{\mathbf{H}}{H} \\ &= \frac{\mathbf{a}_1}{h} \cdot \frac{(h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3)}{H} \\ &= \frac{1}{H}. \end{aligned}$$

Used purely as a geometrical tool, the reciprocal lattice is of considerable help in the solution of many problems in crystal geometry. Consider, for example, the relation between the planes of a zone and the axis of that zone. Since the planes of a zone are all parallel to one line, the zone axis, their normals must be coplanar. This means that planes of a zone are represented, in the reciprocal lattice, by a set of points lying on a plane passing through the origin of the reciprocal lattice. If the plane (*hkl*) belongs to the zone whose axis is [*uvw*], then the normal to (*hkl*), namely, **H**, must be perpendicular to [*uvw*]. Express the zone axis as a vector in the crystal lattice and **H** as a vector in the reciprocal lattice:

$$\text{Zone axis} = u\mathbf{a}_1 + v\mathbf{a}_2 + w\mathbf{a}_3,$$

$$\mathbf{H} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3.$$

If these two vectors are perpendicular, their dot product must be zero:

$$(u\mathbf{a}_1 + v\mathbf{a}_2 + w\mathbf{a}_3) \cdot (h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3) = 0,$$

$$hu + kv + lw = 0.$$

This is the relation given without proof in Sec. 2-6. By similar use of reciprocal-lattice vectors, other problems of crystal geometry, such as the derivation of the plane-spacing equations given in Appendix 1, may be greatly simplified.

A15-4 Diffraction and the reciprocal lattice. The great utility of the reciprocal lattice, however, lies in its connection with diffraction problems. We shall consider how x-rays scattered by the atom O at the origin of the crystal lattice (Fig. A15-7) are affected by those scattered by any other atom A whose coordinates with respect to the origin are $p\mathbf{a}_1$, $q\mathbf{a}_2$ and $r\mathbf{a}_3$, where p, q, and r are integers. Thus,

$$\mathbf{OA} = p\mathbf{a}_1 + q\mathbf{a}_2 + r\mathbf{a}_3.$$

Let the incident x-rays have a wavelength λ, and let the incident and diffracted beams be represented by the unit vectors $\mathbf{S}_0$ and $\mathbf{S}$, respectively. $\mathbf{S}_0$, $\mathbf{S}$, and $\mathbf{OA}$ are, in general, not coplanar.

To determine the conditions under which diffraction will occur, we must determine the phase difference between the rays scattered by the atoms O and A. The lines Ou and Ov in Fig. A15-7 are wave fronts perpendicular to the incident beam $\mathbf{S}_0$ and the diffracted beam $\mathbf{S}$, respectively. Let δ be the path difference for rays scattered by O and A. Then

$$\begin{aligned}\delta &= uA + Av\\ &= Om + On\\ &= \mathbf{S}_0 \cdot \mathbf{OA} + (-\mathbf{S}) \cdot \mathbf{OA}\\ &= -\mathbf{OA} \cdot (\mathbf{S} - \mathbf{S}_0).\end{aligned}$$

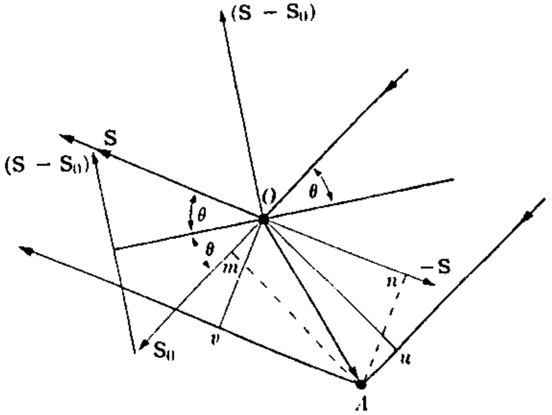


FIG. A15-7. X-ray scattering by atoms at O and A. (After Guinier, *X-Ray Crystallographic Technology*, Hilger & Watts, Ltd., London, 1952.)

The corresponding phase difference is given by

$$\begin{aligned}\phi &= \frac{2\pi\delta}{\lambda}\\ &= -2\pi\left(\frac{\mathbf{S} - \mathbf{S}_0}{\lambda}\right) \cdot \mathbf{OA}.\end{aligned} \tag{6}$$

Diffraction is now related to the reciprocal lattice by expressing the vector $(\mathbf{S} - \mathbf{S}_0)/\lambda$ as a vector in that lattice. Let

$$\frac{\mathbf{S} - \mathbf{S}_0}{\lambda} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3.$$

This is now in the form of a vector in reciprocal space but, at this point, no particular significance is attached to the parameters h, k, and l. They are continuously variable and may assume any values, integral or nonintegral. Equation (6) now becomes

$$\phi = -2\pi(h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3) \cdot (p\mathbf{a}_1 + q\mathbf{a}_2 + r\mathbf{a}_3) = -2\pi(hp + kq + lr).$$

A diffracted beam will be formed only if reinforcement occurs, and this requires that ϕ be an integral multiple of 2π. This can happen only if h, k, and l are integers. Therefore the condition for diffraction is that the vector $(\mathbf{S} - \mathbf{S}_0)/\lambda$ end on a *point* in the reciprocal lattice, or that

$$\boxed{\frac{\mathbf{S} - \mathbf{S}_0}{\lambda} = \mathbf{H} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3}\,, \tag{7}$$

where h, k, and l are now restricted to integral values.

Both the Laue equations and the Bragg law can be derived from Eq. (7). The former are obtained by forming the dot product of each side of the equation and the three crystal-lattice vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ successively. For example,

$$\begin{aligned}\mathbf{a}_1 \cdot \left(\frac{\mathbf{S} - \mathbf{S}_0}{\lambda}\right) &= \mathbf{a}_1 \cdot (h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3)\\ &= h,\end{aligned}$$

or

$$\mathbf{a}_1 \cdot (\mathbf{S} - \mathbf{S}_0) = h\lambda. \tag{8}$$

Similarly,

$$\mathbf{a}_2 \cdot (\mathbf{S} - \mathbf{S}_0) = k\lambda, \tag{9}$$

$$\mathbf{a}_3 \cdot (\mathbf{S} - \mathbf{S}_0) = l\lambda. \tag{10}$$

Equations (8) through (10) are the vector form of the equations derived by von Laue in 1912 to express the necessary conditions for diffraction. They must be satisfied simultaneously for diffraction to occur.

As shown in Fig. A15-7, the vector $(\mathbf{S} - \mathbf{S}_0)$ bisects the angle between the incident beam $\mathbf{S}_0$ and the diffracted beam $\mathbf{S}$. The diffracted beam $\mathbf{S}$ can therefore be considered as being reflected from a set of planes perpendicular to $(\mathbf{S} - \mathbf{S}_0)$. In fact, Eq. (7) states that $(\mathbf{S} - \mathbf{S}_0)$ is parallel to $\mathbf{H}$, which is in turn perpendicular to the planes (hkl). Let θ be the angle between $\mathbf{S}$ (or $\mathbf{S}_0$) and these planes. Then, since $\mathbf{S}$ and $\mathbf{S}_0$ are unit vectors,

$$(S - S_0) = 2 \sin \theta.$$

Therefore

$$\frac{2 \sin \theta}{\lambda} = \frac{S - S_0}{\lambda} = H = \frac{1}{d},$$

or

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

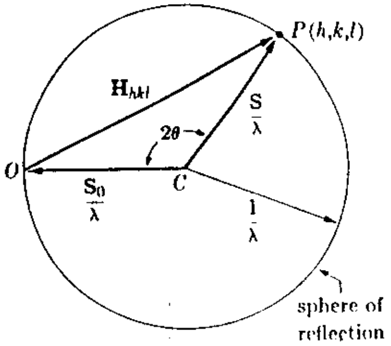


FIG. A15-8. The Ewald construction. Section through the sphere of reflection containing the incident and diffracted beam vectors.

The conditions for diffraction expressed by Eq. (7) may be represented graphically by the "Ewald construction" shown in Fig. A15-8. The vector $\mathbf{S}_0/\lambda$ is drawn parallel to the incident beam and $1/\lambda$ in length. The terminal point O of this vector is taken as the origin of the reciprocal lattice, drawn to the same scale as the vector $\mathbf{S}_0/\lambda$. A sphere of radius $1/\lambda$ is drawn about C, the initial point of the incident-beam vector. Then the condition for diffraction from the (hkl) planes is that the point hkl in the reciprocal lattice (point P in Fig. A15-8) touch the surface of the sphere, and the direction of the diffracted-beam vector $\mathbf{S}/\lambda$ is found by joining C to P. When this condition is fulfilled, the vector $\mathbf{OP}$ equals both $\mathbf{H}_{hkl}$ and $(\mathbf{S} - \mathbf{S}_0)/\lambda$, thus satisfying Eq. (7). Since diffraction depends on a reciprocal-lattice point's touching the surface of the sphere drawn about C, this sphere is known as the "sphere of reflection."

Our initial assumption that p, q, and r are integers apparently excludes all crystals except those having only one atom per cell, located at the cell corners. For if the unit cell contains more than one atom, then the vector $\mathbf{OA}$ from the origin to "any atom" in the crystal may have nonintegral coordinates. However, the presence of these additional atoms in the unit cell affects only the intensities of the diffracted beams, not their directions, and it is only the diffraction directions which are predicted by the Ewald construction. Stated in another way, the reciprocal lattice depends only on the shape and size of the unit cell of the crystal lattice and not at all on the arrangement of atoms within that cell. If we wish to take atom arrangement into consideration, we may weight each reciprocal-lattice point hkl with the appropriate value of the scattering power ($= |F|^2$, where F is the structure factor) of the particular (hkl) planes involved. Some planes may then have zero scattering power, thus eliminating some reciprocal-lattice points from consideration, e.g., all reciprocal-lattice points having odd values of $(h + k + l)$ for body-centered crystals.

The common methods of x-ray diffraction are differentiated by the methods used for bringing reciprocal-lattice points into contact with the surface of the sphere of reflection. The radius of the sphere may be varied by varying the incident wavelength (Laue method), or the position of the reciprocal lattice may be varied by changes in the orientation of the crystal (rotating-crystal and powder methods).

A15-5 The rotating-crystal method. As stated in Sec. 3-6, when monochromatic radiation is incident on a single crystal rotated about one of its axes, the reflected beams lie on the surface of imaginary cones coaxial with the rotation axis. The way in which this reflection occurs may be shown very nicely by the Ewald construction. Suppose a simple cubic crystal is rotated about the axis [001]. This is equivalent to rotation of the reciprocal lattice about the $\mathbf{b}_3$ axis. Figure A15-9 shows a portion of the reciprocal lattice oriented in this manner, together with the adjacent sphere of reflection.

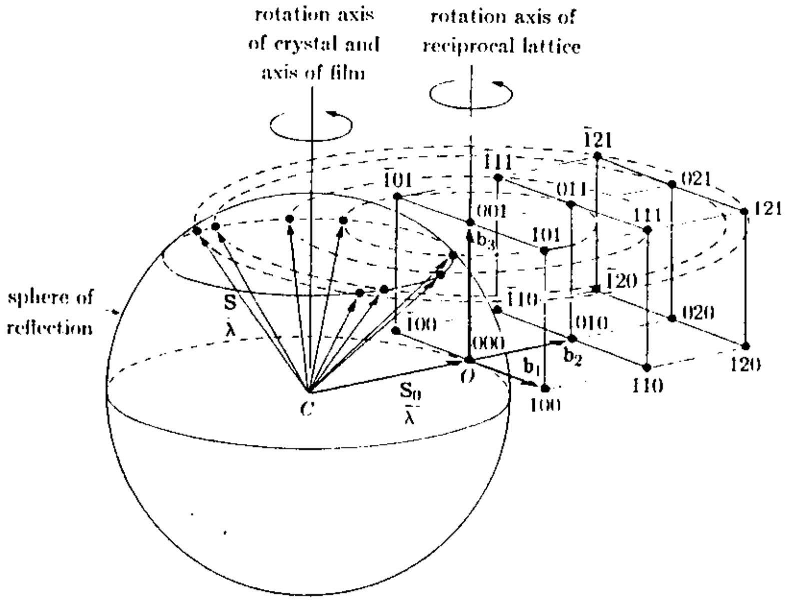


FIG. A15-9. Reciprocal-lattice treatment of rotating-crystal method.

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All crystal planes having indices $(hk1)$ are represented by points lying on a plane (called the "$l = 1$ layer") in the reciprocal lattice, normal to $\mathbf{b}_3$. When the reciprocal lattice rotates, this plane cuts the reflection sphere in the small circle shown, and any points on the $l = 1$ layer which touch the sphere surface must touch it on this circle. Therefore all diffracted-beam vectors $\mathbf{S}/\lambda$ must end on this circle, which is equivalent to saying that the diffracted beams must lie on the surface of a cone. In this particular case, all the $hk1$ points shown intersect the surface of the sphere sometime during their rotation about the $\mathbf{b}_3$ axis, producing the diffracted beams shown in Fig. A15-9. In addition many $hk0$ and $hk\bar{1}$ reflections would be produced, but these have been omitted from the drawing for the sake of clarity.

This simple example may suggest how the rotation photograph of a crystal of unknown structure, and therefore having an unknown reciprocal lattice, can yield clues as to the distribution in space of reciprocal-lattice points. By taking a number of photographs with the crystal rotated successively about various axes, the crystallographer gradually discovers the complete distribution of reflecting points. Once the reciprocal lattice is known, the crystal lattice is easily derived, because it is a corollary of Eqs. (1) through (3) that the reciprocal of the reciprocal lattice is the crystal lattice.

A15-6 The powder method. The random orientations of the individual crystals in a powder specimen are equivalent to the rotation of a single crystal about all possible axes during the x-ray exposure. The reciprocal lattice therefore takes on all possible orientations relative to the incident beam, but its origin remains fixed at the end of the $\mathbf{S}_0/\lambda$ vector.

Consider any point hkl in the reciprocal lattice, initially at P_1 (Fig. A15-10). This point can be brought into a reflecting position on the surface of the reflection sphere by a rotation of the lattice about an axis through O and normal to OC, for example. Such a rotation would move P_1 to P_2. But the point hkl can still remain on the surface of the sphere [i.e., reflection will still occur from the same set of planes (hkl)] if the reciprocal lattice is then rotated about the axis OC, since the point hkl will then move around the small circle P_2P_3. During this motion, the $\mathbf{H}$ vector sweeps out a cone whose apex is at O, and the diffracted beams all lie on the surface of another cone whose apex is at C. The axes of both cones coincide with the incident beam.

The number of different hkl reflections obtained on a powder photograph depends, in part, on the relative magnitudes of the wavelength and the crystal-lattice parameters or, in reciprocal-lattice language, on the relative sizes of the sphere of reflection and the reciprocal-lattice unit cell. To find the number of reflections we may regard the reciprocal lattice as fixed and the incident-beam vector $\mathbf{S}_0/\lambda$ as rotating about its terminal point through all possible positions. The reflection sphere therefore swings about the origin of the reciprocal lattice and sweeps out a sphere of radius $2/\lambda$, called the "limiting sphere" (Fig. A15-11). All reciprocal-lattice points within the limiting sphere can touch the surface of the reflection sphere and cause reflection to occur.

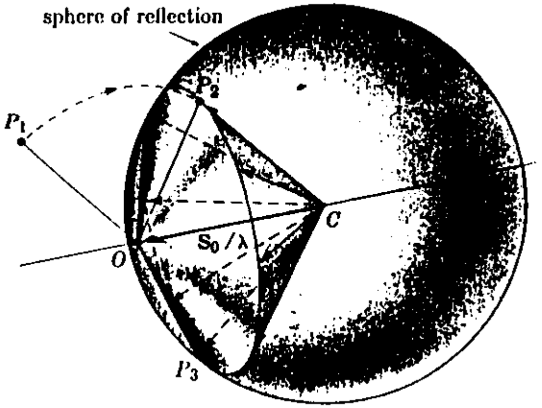

FIG. A15-10. Formation of a cone of diffracted rays in the powder method.

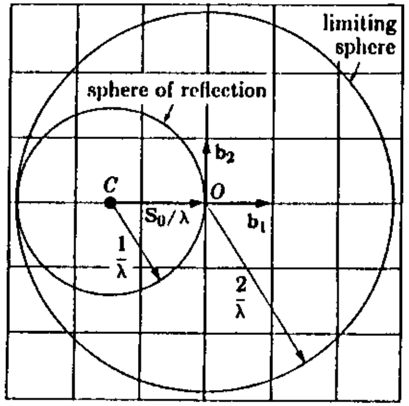

FIG. A15-11. The limiting sphere for the powder method.

It is also a corollary of Eqs. (1) through (3) that the volume v of the reciprocal-lattice unit cell is the reciprocal of the volume V of the crystal unit cell. Since there is one reciprocal-lattice point per cell of the reciprocal lattice, the number of reciprocal-lattice points within the limiting sphere is given by

$$n = \frac{(4\pi/3)(2/\lambda)^3}{v} = \frac{32\pi V}{3\lambda^3}. \tag{11}$$

Not all of these n points will cause a separate reflection: some of them may have a zero structure factor, and some may be at equal distances from the reciprocal-lattice origin, i.e., correspond to planes of the same spacing. (The latter effect is taken care of by the multiplicity factor, since this gives the number of different planes in a form having the same spacing.) However, Eq. (11) may always be used directly to obtain an upper limit to the number of possible reflections. For example, if $V = 50\text{A}^3$ and $\lambda = 1.54\text{A}$, then $n = 460$. If the specimen belongs to the triclinic system, this number will be reduced by a factor of only 2, the multiplicity factor, and the powder photograph will contain 230 separate diffraction lines! As the symmetry of the crystal increases, so does the multiplicity factor and the fraction of reciprocal-lattice points which have zero structure factor, resulting in a decrease in the number of diffraction lines. For example, the powder pattern of a diamond cubic crystal has only 5 lines, for the same values of V and λ assumed above.

A15-7 The Laue method. Diffraction occurs in the Laue method because of the continuous range of wavelengths present in the incident beam. Stated alternatively, contact between a fixed reciprocal-lattice point and the sphere of reflection is produced by continuously varying the radius of the sphere. There is therefore a whole set of reflection spheres, not just one; each has a different center, but all pass through the origin of the reciprocal lattice. The range of wavelengths present in the incident beam is of course not infinite. It has a sharp lower limit at λ_{SWL}, the short-wavelength limit of the continuous spectrum; the upper limit is less definite but is often taken as the wavelength of the *K* absorption edge of the silver in the emulsion (0.48A), because the effective photographic intensity of the continuous spectrum drops abruptly at that wavelength [see Fig. 1-18(c)].

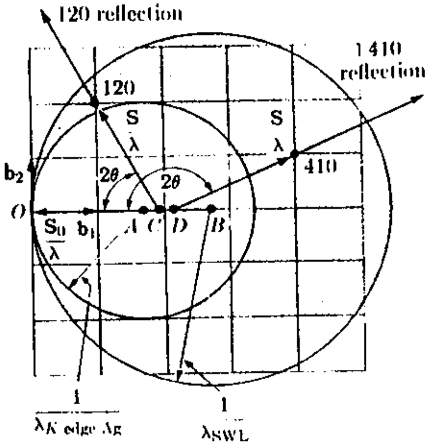

FIG. A15-12. Reciprocal-lattice treatment of the Laue method. $(\mathbf{S}-\mathbf{S}_0)/\lambda = \mathbf{H}$.

To these two extreme wavelengths correspond two extreme reflection spheres, as shown in Fig. A15-12, which is a section through these spheres and the $l = 0$ layer of a reciprocal lattice. The incident beam is along the $\mathbf{b}_1$ vector, i.e., perpendicular to the (h00) planes of the crystal. The larger sphere shown is centered at *B* and has a radius equal to the reciprocal of λ_{SWL}, while the smaller sphere is centered at *A* and has a radius equal to the reciprocal of the wavelength of the silver *K* absorption edge.

There is a whole series of spheres lying between these two and centered on the line segment *AB*. Therefore any reciprocal-lattice point lying in the shaded region of the diagram is on the surface of one of these spheres and corresponds to a set of crystal planes oriented to reflect one of the incident wavelengths. In the forward direction, for example, a 120 reflection will be produced. To find its direction, we locate a point *C* on *AB* which is equidistant from the origin *O* and the reciprocal-lattice point 120; *C* is therefore the center of the reflection sphere passing through the point 120. Joining *C* to 120 gives the diffracted-beam vector $\mathbf{S}/\lambda$ for this reflection. The direction of the 410 reflection, one of the many backward-reflected beams, is found in similar fashion; here the reciprocal-lattice point in question is situated on a reflection sphere centered at *D*.

There is another way of treating the Laue method which is more convenient for many purposes. The basic diffraction equation, Eq. (7), is rewritten in the form

$$\boxed{\mathbf{S}-\mathbf{S}_0 = \lambda \mathbf{H}}. \tag{12}$$

Both sides of this equation are now dimensionless and the radius of the sphere of reflection is simply unity, since $\mathbf{S}$ and $\mathbf{S}_0$ are unit vectors. But the position of the reciprocal-lattice points is now dependent on the wavelength used, since their distance from the origin of the reciprocal lattice is now given by λH.

In the Laue method, each reciprocal-lattice point (except 0 0 0) is drawn out into a line segment directed to the origin, because of the range of wavelengths present in the incident beam. The result is shown in Fig. A15-13,* which is drawn to correspond to Fig. A15-12. The point nearest the origin on each line segment has a value of λH corresponding to the shortest wavelength present, while the point on the other end has a value of λH corresponding to the longest effective wavelength. Thus the 100 reciprocal-lattice line extends from *A* to *B*, where $OA = \lambda_{\min} H_{100}$ and $OB = \lambda_{\max} H_{100}$. Since the length of any line increases as H increases, for a given range of wavelengths, overlapping occurs for the higher orders, as shown by 200, 300, 400, etc. The reflection sphere is drawn with unit radius, and reflection occurs whenever a reciprocal-lattice line intersects the sphere surface. Graphically, the advantage of this construction over that of Fig. A15-12 is that all diffracted beams are now drawn from the same point *C*, thus facilitating the comparison of the diffraction angles 2θ for different reflections.

This construction also shows why the diffracted beams from planes of a zone are arranged on a cone in the Laue method. All reciprocal-lattice lines representing the planes of one zone lie on a plane passing through

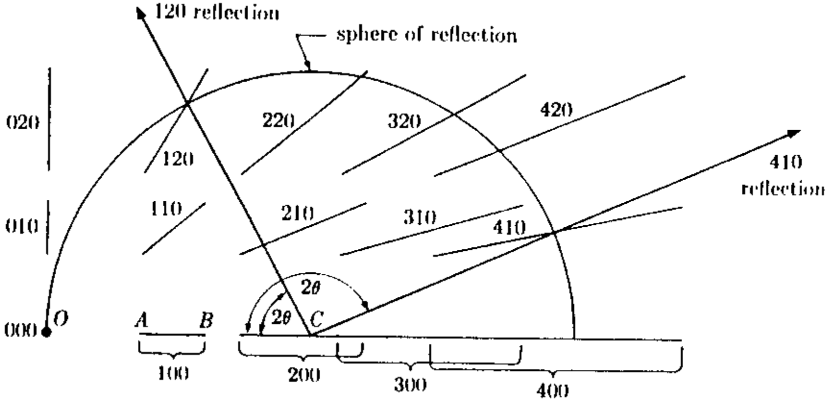

FIG. A15-13. Alternate reciprocal-lattice treatment of the Laue method. $\mathbf{S}-\mathbf{S}_0 = \lambda \mathbf{H}$.

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* In this figure, as well as in Figs. A15-11 and A15-12, the size of the reciprocal lattice, relative to the size of the reflection sphere, has been exaggerated for clarity.

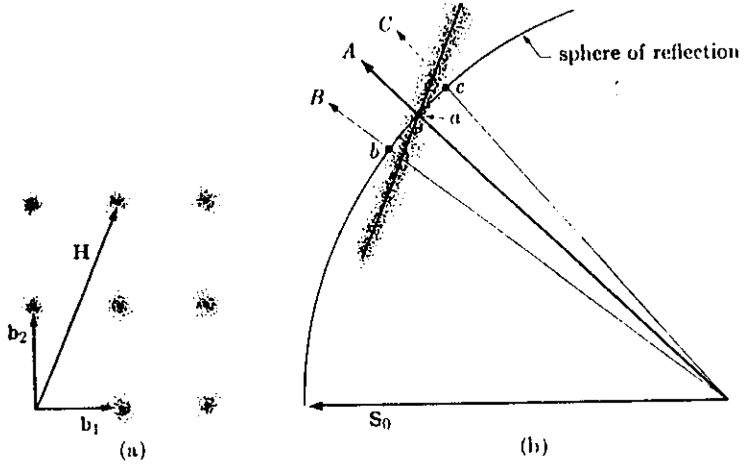

FIG. A15-14. The effect of thermal vibration on the reciprocal lattice.

the origin of the reciprocal lattice. This plane cuts the reflection sphere in a circle, and all the diffracted beam vectors S must end on this circle, thus producing a conical array of diffracted beams, the axis of the cone coinciding with the zone axis.

Another application of this construction, to the problem of temperature-diffuse scattering, will illustrate the general utility of the reciprocal-lattice method in treating diffuse scattering phenomena. The reciprocal lattice of any crystal may be regarded as a distribution of "scattered intensity" in reciprocal space, in the sense that a scattered beam will be produced whenever the sphere of reflection intersects a point in reciprocal space where the "scattered intensity" is not zero. If the crystal is perfect, the scattered intensity is concentrated at points in reciprocal space, the points of the reciprocal lattice, and is zero everywhere else. But if anything occurs to disturb the regularity of the crystal lattice, then these points become smeared out, and appreciable scattered intensity exists in regions of reciprocal space where h, k, and l are nonintegral. For example, if the atoms of the crystal are undergoing thermal vibration, then each point of the reciprocal lattice spreads out into a region which may be considered, to a first approximation, as roughly spherical in shape, as suggested by Fig. A15-14(a). In other words, the thermally produced elastic waves which run through the crystal lattice so disturb the regularity of the atomic planes that the corresponding H vectors end, not on points, but in small spherical regions. The scattered intensity is not distributed uniformly within each region: it remains very high at the central point, where h, k, and l are integral, and is very weak and diffuse in the surrounding volume, as indicated in the drawing.

FIG. A15-15. Transmission Laue pattern showing thermal asterism. Aluminum crystal, 280°C, 5 min exposure.

What then will be the effect of thermal agitation on, for example, a transmission Laue pattern? If we use the construction of Fig. A15-13, i.e., if we make distances in the reciprocal lattice equal to λH, then each spherical volume in the reciprocal lattice will be drawn out into a rod, roughly cylindrical in shape and directed to the origin, as indicated in Fig. A15-14(b), which is a section through the reflection sphere and one such rod. The axis of each rod is a line of high intensity and this is surrounded by a low-intensity region. This line intersects the reflection sphere at a and produces the strong diffracted beam A, the ordinary Laue reflection. But on either side of A there are weak scattered rays, extending from B to C, due to the intersection, extending from b to c, of the diffuse part of the rod with the sphere of reflection. In a direction normal to the drawing, however, the diffuse rod intersects the sphere in an arc equal only to the rod diameter, which is much shorter than the arc bc. We are thus led to expect, on a film placed in the transmission position, a weak and diffuse streak running *radially* through the usual sharp, intense Laue spot.

Figure A15-15 shows an example of this phenomenon, often called thermal asterism because of the radial direction of the diffuse streaks. This photograph was obtained from aluminum at 280°C in 5 minutes. Actually, thermal agitation is quite pronounced in aluminum even at room temperature, and thermal asterism is usually evident in overexposed room-temperature photographs. Even in Fig. 3-6(a), which was given a normal exposure of about 15 minutes, radial streaks are faintly visible. In this latter photograph, there is a streak near the center which does not pass through any Laue spot: it is due to a reciprocal-lattice rod so nearly tangent to the reflection sphere that the latter intersects only the diffuse part of the rod and not its axis.