APPENDIX 1
THE RECIPROCAL LATTICE

A1-1 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.

A1-2 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. A1-1 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 the absolute value of the vector.
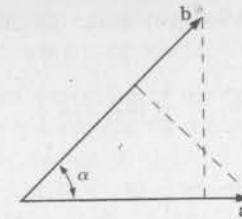
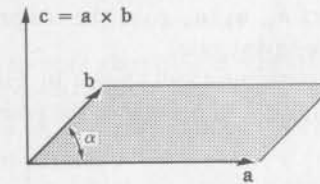Fig. A1-1 Scalar product of two vectors.

Fig. A1-2 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. A1-2. 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

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

A1-3 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

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

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

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

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.

Consider the general triclinic unit cell shown in Fig. A1–3. 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

Fig. A1–3 Location of the reciprocal-lattice axis $\mathbf{b}_3$.

$\mathbf{b}_1$ 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

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

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. A1–4 and A1–5 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 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. A1–4 and A1–5, four cells of the reciprocal lattice are shown, together with two $\mathbf{H}$ vectors in each case. By means of the scales shown, it may be verified that each $\mathbf{H}$ 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 sponding planes and normal to them. Note that reciprocal lattice points such as
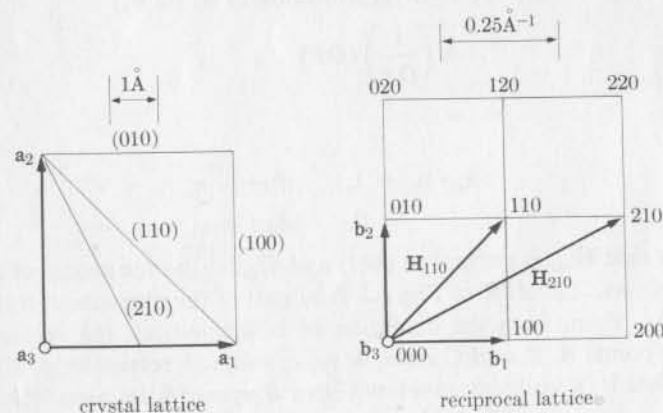

crystal lattice   reciprocal lattice

Fig. A1–4 The reciprocal lattice of a cubic crystal which has $a_1 = 4$ Å. The axes $\mathbf{a}_3$ and $\mathbf{b}_3$ are normal to the drawing.
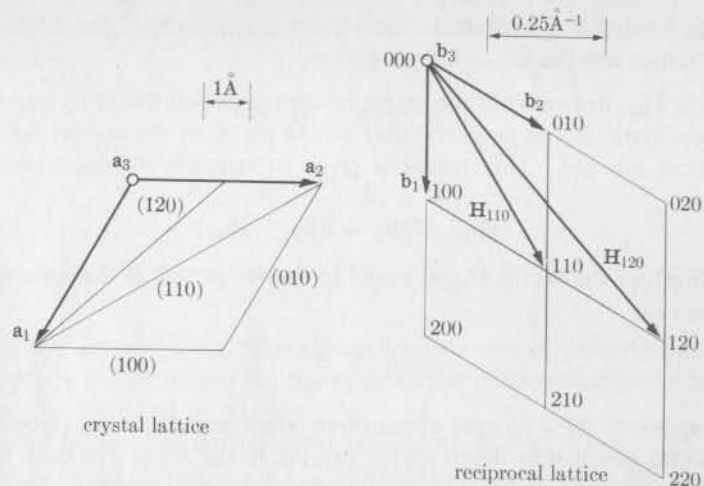
Fig. A1-5 The reciprocal lattice of a hexagonal crystal which has $a_1 = 4$ Å. (Here the three-symbol system of plane indexing is used and a_3 is the axis usually designated c.) The axes a_3 and b_3 are normal to the drawing.

nh, nk, nl, where n is an integer, correspond to planes parallel to (hkl) and having $1/n$ their spacing. Thus, H_{220} is perpendicular to (220) planes and therefore parallel to H_{110}, since (110) and (220) are parallel, but H_{220} is twice as long as 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 b_3, for example, is normal to both a_1 and a_2, its dot product with either one of these vectors is zero, or

$$b_3 \cdot a_1 = b_3 \cdot a_2 = 0.$$

The dot product of b_3 and a_3, however, is unity, since (see Fig. A1-3)

$$b_3 \cdot a_3 = (b_3) \text{ (projection of } a_3 \text{ on } b_3)$$

$$= \left(\frac{1}{OP}\right)(OP)$$

$$= 1.$$

In general,

$$a_m \cdot b_n = 1, \quad \text{if } m = n, \tag{4}$$

$$= 0, \quad \text{if } m \neq n. \tag{5}$$

The fact that H_{hkl} is normal to (hkl) and H_{hkl} is the reciprocal of d_{hkl} may be proved as follows. Let ABC of Fig. A1-6 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 a_1/h, a_2/k, and a_3/l, respectively. Consider the vector AB, that is, a vector drawn from A to B, lying in the plane (hkl). Since

$$\frac{a_1}{h} + AB = \frac{a_2}{k},$$

then

$$AB = \frac{a_2}{k} - \frac{a_1}{h}.$$

Forming the dot product of H and AB, we have

$$H \cdot AB = (hb_1 + kb_2 + lb_3) \cdot \left(\frac{a_2}{k} - \frac{a_1}{h}\right).$$

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

$$H \cdot AB = 1 - 1 = 0.$$

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

$$d = ON = \frac{a_1}{h} \cdot n.$$

But

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

Therefore

$$d = \frac{a_1}{h} \cdot \frac{H}{H}$$

$$= \frac{a_1}{h} \cdot \frac{(hb_1 + kb_2 + lb_3)}{H}$$
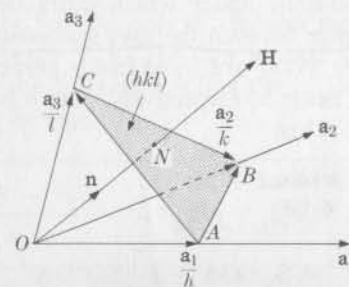
$$= \frac{1}{H}.$$

Fig. A1-6 Relation between reciprocal-lattice vector H and crystal plane (hkl).

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, $\mathbf{H}$, must be perpendicular to $[uvw]$. Express the zone axis as a vector in the crystal lattice and $\mathbf{H}$ 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 3, may be greatly simplified.

A1-4 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. A1–7) 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. A1–7 are wave fronts perpendicular to the incident beam $\mathbf{S}_0$ and the scattered beam $\mathbf{S}$, respectively. Let δ be the path difference for rays scattered by O and A. Then

$$\delta = uA + Av$$

$$= Om + On$$

$$= \mathbf{S}_0 \cdot \mathbf{OA} + (-\mathbf{S}) \cdot \mathbf{OA}$$

$$= -\mathbf{OA} \cdot (\mathbf{S} - \mathbf{S}_0).$$
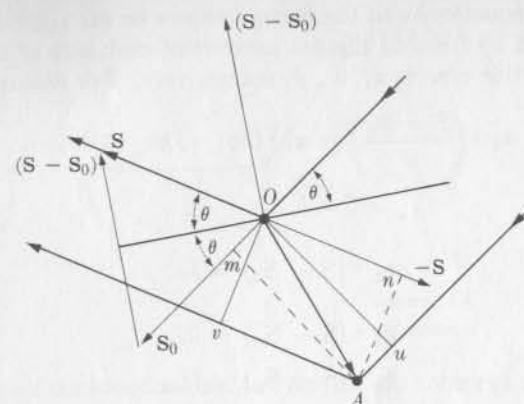
Fig. A1–7 X-ray scattering by atoms at O and A. After Guinier [G.10].

The corresponding phase difference, in radians, is given by

$$\phi = \frac{2\pi\delta}{\lambda}$$

$$= -2\pi \left(\frac{\mathbf{S} - \mathbf{S}_0}{\lambda} \right) \cdot \mathbf{OA}. \tag{6}$$

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,

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

$$= h,$$

or

Similarly,

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

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

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

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. A1–7, 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,

$$(\mathbf{S} - \mathbf{S}_0) = 2 \sin \theta.$$

Therefore

$$\frac{2 \sin \theta}{\lambda} = \frac{\mathbf{S} - \mathbf{S}_0}{\lambda} = H = \frac{1}{d},$$

or

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

The conditions for diffraction expressed by Eq. (7) may be represented graphically by the "Ewald construction" shown in Fig. A1–8. 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. A1–8) 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 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
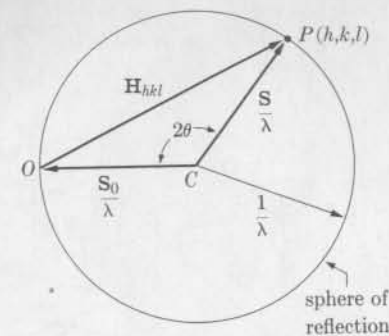
Fig. A1–8 The Ewald construction. Section through the sphere of reflection containing the incident and diffracted beam vectors.

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).

A1–5 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 A1–9 shows a portion of the reciprocal lattice oriented in this manner, together with the adjacent sphere of reflection.

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
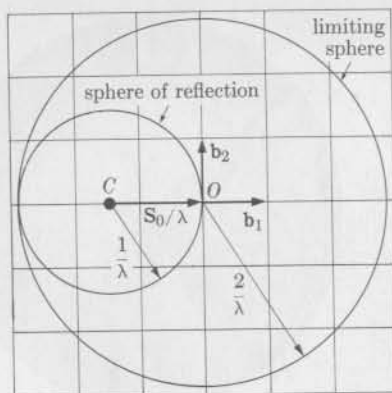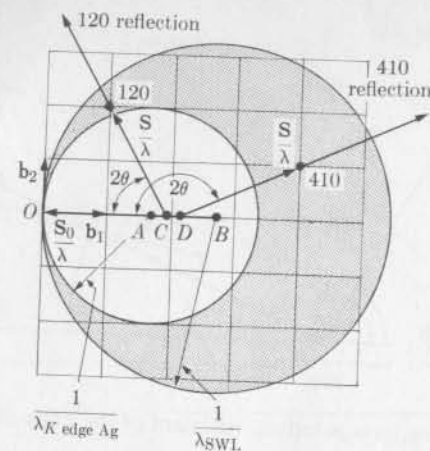
Fig. A1–9 Reciprocal-lattice treatment of rotating-crystal method.

touch it on this circle. Therefore all diffracted-beam vectors S/λ must end on this circle, which is equivalent to saying that the diffracted beams must lie on the surface of a cone. In this particular case, all the $hk1$ points shown intersect the surface of the sphere sometime during their rotation about the b_3 axis, producing the diffracted beams shown in Fig. A1–9. 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.

A1-6 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 S_0/λ vector.

Consider any point hkl in the reciprocal lattice, initially at P_1 (Fig. A1–10). This point can be brought into a reflecting position on the surface of the reflection

Fig. A1–10 Formation of a cone of diffracted rays in the powder method.

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 S_0/λ 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. A1–11). All reciprocal-lattice points within the limiting sphere can touch the surface of the reflection sphere and cause reflection to occur.

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

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

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

Fig. A1–11 The limiting sphere for the powder method.

Fig. A1–12 Reciprocal-lattice treatment of the Laue method. $(S - S_0)/\lambda = H$.

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 $V = 50 \text{ Å}^3$ and $\lambda = 1.54 \text{ Å}$, 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 element has only 5 lines, for the same values of V and λ assumed above.

A1-7 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 (0.48 Å), because the effective photographic intensity of the continuous spectrum drops abruptly at that wavelength [see Fig. 1–19(c)].

To these two extreme wavelengths correspond two extreme reflection spheres, as shown in Fig. A1–12, which is a section through these spheres and the $l = 0$ layer of a reciprocal lattice. The incident beam is along the 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 S/λ 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

$$S - S_0 = \lambda H .$$

(12)

Both sides of this equation are now dimensionless and the radius of the sphere of reflection is simply unity, since S and 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 000) 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. A1–13,* which is drawn to correspond to Fig. A1–12. The point nearest the origin on each line segment has

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* In this figure, as well as in Figs. A1–11 and A1–12, the size of the reciprocal lattice, relative to the size of the reflection sphere, has been exaggerated for clarity.
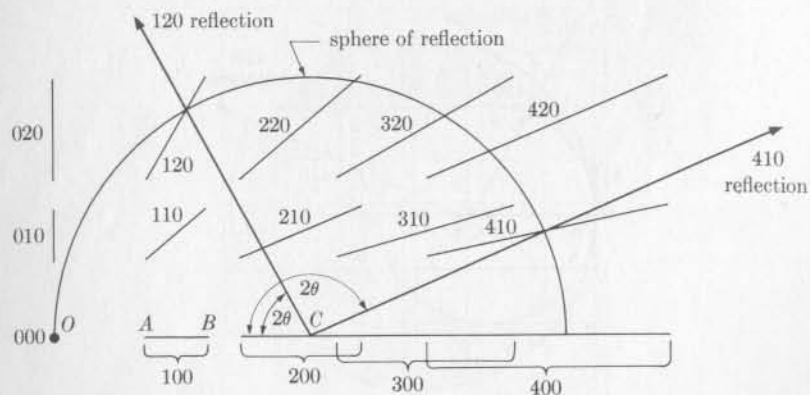
Fig. A1–13 Alternative reciprocal-lattice treatment of the Laue method. $\mathbf{S} - \mathbf{S}_0 = \lambda \mathbf{H}$.

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. A1–12 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 the origin of the reciprocal lattice. This plane cuts the reflection sphere in a circle, and all the diffracted beam vectors $\mathbf{S}$ 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. A1–14(a). In other words, the
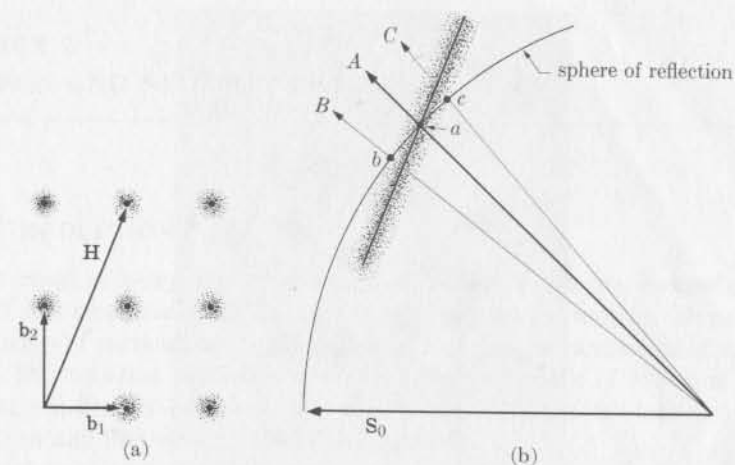
Fig. A1–14 The effect of thermal vibration on the reciprocal lattice.

thermally produced elastic waves which run through the crystal lattice so disturb the regularity of the atomic planes that the corresponding $\mathbf{H}$ 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.

What then will be the effect of thermal agitation on, for example, a transmission Laue pattern? If we use the construction of Fig. A1–13, 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. A1–14(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 A1–15 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
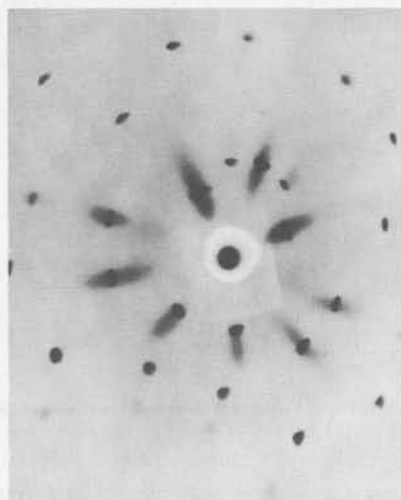
Fig. A1–15 Transmission Laue pattern showing thermal asterism. Aluminum crystal, 280°C, 5 min exposure.

faintly visible. In this latter photograph, there is a streak near the center that does not pass through any Laue spot: it is due to a reciprocal-lattice rod so nearly tangent to the reflection sphere that the sphere intersects only the diffuse part of the rod and not its axis.

The enlargement of reciprocal-lattice points caused by thermal vibration, depicted in Fig. A1–14(a), is not observed in powder patterns. It is so weak and diffuse that it is lost in the background.

APPENDIX 2
ELECTRON AND NEUTRON DIFFRACTION

A2–1 INTRODUCTION

Just as a beam of x-rays has a dual wave-particle character so, inversely, does a stream of particles have certain properties peculiar to wave motion. In particular, such a stream of particles can be diffracted by a periodic arrangement of scattering centers. This was first predicted theoretically by de Broglie in 1924 and demonstrated experimentally by Davisson and Germer in 1927 (for electrons) and by Von Halban and Preiswerk in 1936 (for neutrons).

If a stream of particles can behave like wave motion, it must have a wavelength associated with it. The theory of wave mechanics indicates that this wavelength is given by the ratio of Planck's constant h to the momentum of the particle, or

$$\lambda = \frac{h}{mv},\tag{1}$$

where m is the mass and v the velocity of the particle. If a stream of particles is directed at a crystal under the proper conditions, diffraction will occur in accordance with the Bragg law just as for x-rays, and the directions of diffraction can be predicted by the use of that law and the wavelength calculated from Eq. (1). Both electrons and neutrons have proved to be useful particles for the study of crystalline structure by diffraction and numerous applications of these techniques have been found in metallurgy and in solid state physics and chemistry. The differences between x-ray, electron, and neutron diffraction by crystals are such that these three techniques supplement one another to a remarkable degree, each giving a particular kind of information which the others are incapable of supplying.

A2–2 ELECTRON DIFFRACTION

A stream of fast electrons is obtained in a tube operating on much the same principles as an x-ray tube. The wavelength associated with the electrons depends on the applied voltage, since the kinetic energy of the electrons is given by

$$\tfrac{1}{2}mv^2 = eV,\tag{2}$$

where e is the charge on the electron and V the applied voltage. Combination of Eqs. (1) and (2) shows the inverse relation between wavelength and voltage:

$$\lambda = \sqrt{\frac{150}{V}},$$

where λ is in angstroms and the applied voltage V is in volts. This equation requires small relativistic corrections at high voltages, due to the variation of electron mass