Reciprocal Lattice Vector

To proceed further with the Fourier analysis of the electron concentration we must find the vectors $\mathbf{G}$ of the Fourier sum $\Sigma n_{\mathbf{G}} \exp(i\mathbf{G} \cdot \mathbf{r})$ as in (9).

We construct the axis vectors $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ of the **reciprocal lattice**: 倒晶格

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3}; \qquad \mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3}; \qquad \mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3}. \tag{13}$$

If $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ are primitive vectors of the crystal lattice, then $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ are **primitive vectors of the reciprocal lattice**. Each vector defined by (13) is orthogonal to two axis vectors of the crystal lattice. Thus $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ have the property

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij}, \tag{14}$$

where $\delta_{ij} = 1$ if $i = j$ and $\delta_{ij} = 0$ if $i \neq j$.

Points in the reciprocal lattice are mapped by the set of vectors

$$\mathbf{G} = v_1\mathbf{b}_1 + v_2\mathbf{b}_2 + v_3\mathbf{b}_3, \tag{15}$$

where v_1, v_2, v_3 are integers. A vector $\mathbf{G}$ of this form is a **reciprocal lattice** vector.

倒晶格向量

Reciprocal Lattice 倒晶格

1. Every crystal has two lattices associated with it :
   the crystal lattice, and the reciprocal lattice.
   晶體晶格　　倒晶格

2. The reciprocal lattice is a lattice in the Fourier space associated with the crystal.

3. A diffraction pattern of crystal is a map of the reciprocal lattice of the crystal.

The vectors $\mathbf{G}$ in the Fourier series (9) are just the reciprocal lattice vectors (15), for then the Fourier series representation of the electron density has the desired invariance under any crystal translation $\mathbf{T} = u_1\mathbf{a}_1 + u_2\mathbf{a}_2 + u_3\mathbf{a}_3$. From (9),

$$n(\mathbf{r} + \mathbf{T}) = \sum_{\mathbf{G}} n_{\mathbf{G}} \exp(i\mathbf{G} \cdot \mathbf{r}) \exp(i\mathbf{G} \cdot \mathbf{T}) \ . \tag{16}$$

But $\exp(i\mathbf{G} \cdot \mathbf{T}) = 1$, because

$$\begin{aligned} \exp(i\mathbf{G} \cdot \mathbf{T}) &= \exp[i(v_1\mathbf{b}_1 + v_2\mathbf{b}_2 + v_3\mathbf{b}_3) \cdot (u_1\mathbf{a}_1 + u_2\mathbf{a}_2 + u_3\mathbf{a}_3)] \\ &= \exp[i2\pi(v_1u_1 + v_2u_2 + v_3u_3)] \ . \end{aligned} \tag{17}$$

The argument of the exponential has the form $2\pi i$ times an integer, because $v_1u_1 + v_2u_2 + v_3u_3$ is an integer, being the sum of products of integers. Thus by (9) we have the desired invariance, $n(\mathbf{r} + \mathbf{T}) = n(\mathbf{r}) = \sum n_{\mathbf{G}} \exp(i\mathbf{G} \cdot \mathbf{r})$.

This result proves that the Fourier representation of a function periodic in the crystal lattice can contain components $n_G \exp(iG \cdot r)$ only at the reciprocal lattice vectors G as defined by (15).

Diffraction Conditions

Theorem. The set of reciprocal lattice vectors **G** determines the possible x-ray reflections.

We see in Fig. 6 that the difference in phase factors is $\exp[i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}]$ between beams scattered from volume elements **r** apart.

The total amplitude of the scattered wave in the direction of $\mathbf{k}'$ is proportional to the integral over the crystal of $n(\mathbf{r})\, dV$ times the phase factor $\exp[i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}]$.

the quantity F that we call the **scattering amplitude**:

$$F = \int dV\, n(\mathbf{r}) \exp[i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}] = \int dV\, n(\mathbf{r}) \exp(-i\Delta\mathbf{k} \cdot \mathbf{r}) \ , \qquad (18)$$

where $\mathbf{k} - \mathbf{k}' = -\Delta\mathbf{k}$, or

$$\mathbf{k} + \Delta\mathbf{k} = \mathbf{k}' \ . \qquad (19)$$

Here $\Delta\mathbf{k}$ measures the change in wavevector and is called the **scattering vector** (Fig. 7).

Bragg angle $\theta = \varphi$; $\varphi + \phi = 90°$; $\sin\varphi = \cos\phi$

$k \bullet r = kr\cos\phi = k\,r\sin\varphi = k\,r\sin\theta$

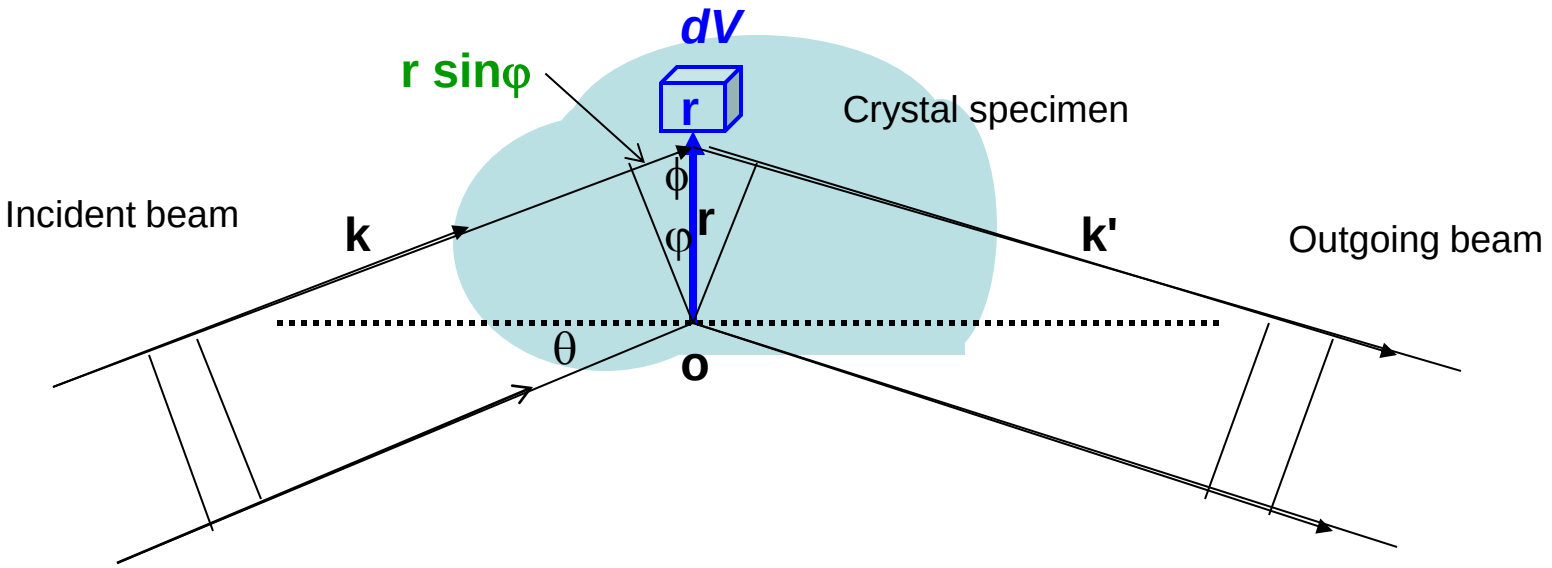


Figure 6 The difference in path length of the incident wave **k** at the points O, **r** is $r \sin \varphi$, and the difference in phase angle is $(2\pi r \sin \varphi)/\lambda$, which is equal to $\mathbf{k} \cdot \mathbf{r}$. For the diffracted wave the difference in phase angle is $-\mathbf{k}' \cdot \mathbf{r}$. The total difference in phase angle is $(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}$, and the wave scattered from dV at **r** has the phase factor $\exp[i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}]$ relative to the wave scattered from a volume element at the origin O.

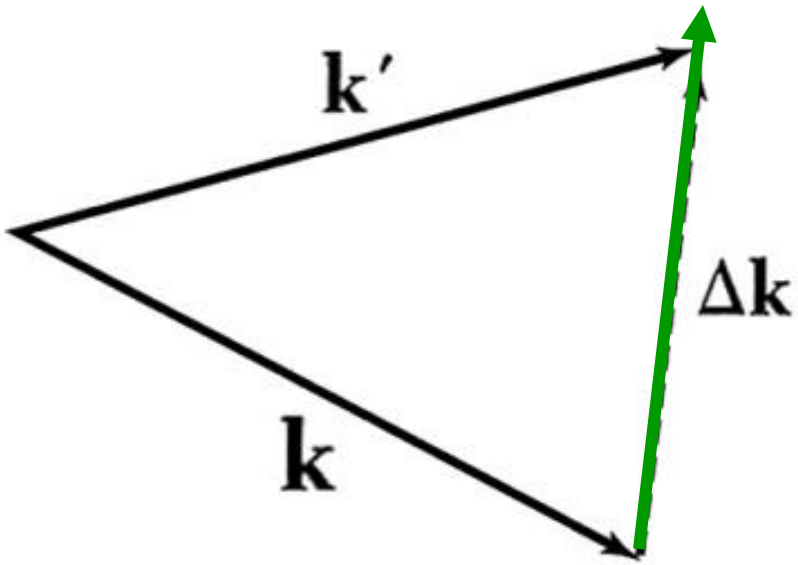


Figure 7 Definition of the scattering vector $\Delta\mathbf{k}$ such that $\mathbf{k} + \Delta\mathbf{k} = \mathbf{k}'$. In elastic scattering the magnitudes satisfy $k' = k$. Further, in Bragg scattering from a periodic lattice, any allowed $\Delta\mathbf{k}$ must equal some reciprocal lattice vector $\mathbf{G}$.

We introduce into (18) the Fourier components (9) of $n(\mathbf{r})$ to obtain for the scattering amplitude

$$F = \sum_{\mathbf{G}} \int dV \, n_{\mathbf{G}} \exp[i(\mathbf{G} - \Delta\mathbf{k}) \cdot \mathbf{r}] \ . \tag{20}$$

When the scattering vector $\Delta\mathbf{k}$ is equal to a particular reciprocal lattice vector,

And F is ~ 0 when $\Delta\mathbf{k} \neq \mathbf{G}$

$$\Delta\mathbf{k} = \mathbf{G} \tag{21}$$

the argument of the exponential vanishes and $F = Vn_G$.

In elastic scattering of a photon its energy $\hbar\omega$ is conserved,

Thus the magnitudes k and k' are equal, and $k^2 = k'^2$, a result that holds also for elastic scattering of electron and neutron beams.

$\mathbf{k} + \mathbf{G} = \mathbf{k}'$, so that the **diffraction condition** is written as $(\mathbf{k} + \mathbf{G})^2 = k^2$, or

$$2\mathbf{k} \cdot \mathbf{G} + \mathbf{G}^2 = 0 \tag{22}$$

This is the central result of the theory of elastic scattering of waves in a periodic lattice.

$$2\mathbf{k} \cdot \mathbf{G} = G^2 \tag{23}$$

This particular expression is often used as the condition for diffraction.

Equation (23) is another statement of the Bragg condition (1). The result of Problem 1 is that the spacing $d(hkl)$ between parallel lattice planes that are normal to the direction $\mathbf{G} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$ is $d(hkl) = 2\pi/|\mathbf{G}|$. Thus the result $2\mathbf{k} \cdot \mathbf{G} = G^2$ may be written as

$$2(2\pi/\lambda) \sin\theta = 2\pi/d(hkl) \ , \quad |\mathbf{G}| = 2\pi/d$$

or $2d(hkl) \sin\theta = \lambda$. Here θ is the angle between the incident beam and the crystal plane.

The integers hkl that define $\mathbf{G}$ are not necessarily identical with the indices of an actual crystal plane, because the hkl may contain a common factor n, whereas in the definition of the indices in Chapter 1 the common factor has been eliminated. We thus obtain the Bragg result:

$$2d \sin\theta = n\lambda \ , \tag{24}$$

where d is the spacing between adjacent parallel planes with indices h/n, k/n, l/n.

Laue Equations

The original result (21) of diffraction theory, namely that $\Delta\mathbf{k} = \mathbf{G}$, may be expressed in another way to give what are called the Laue equations.

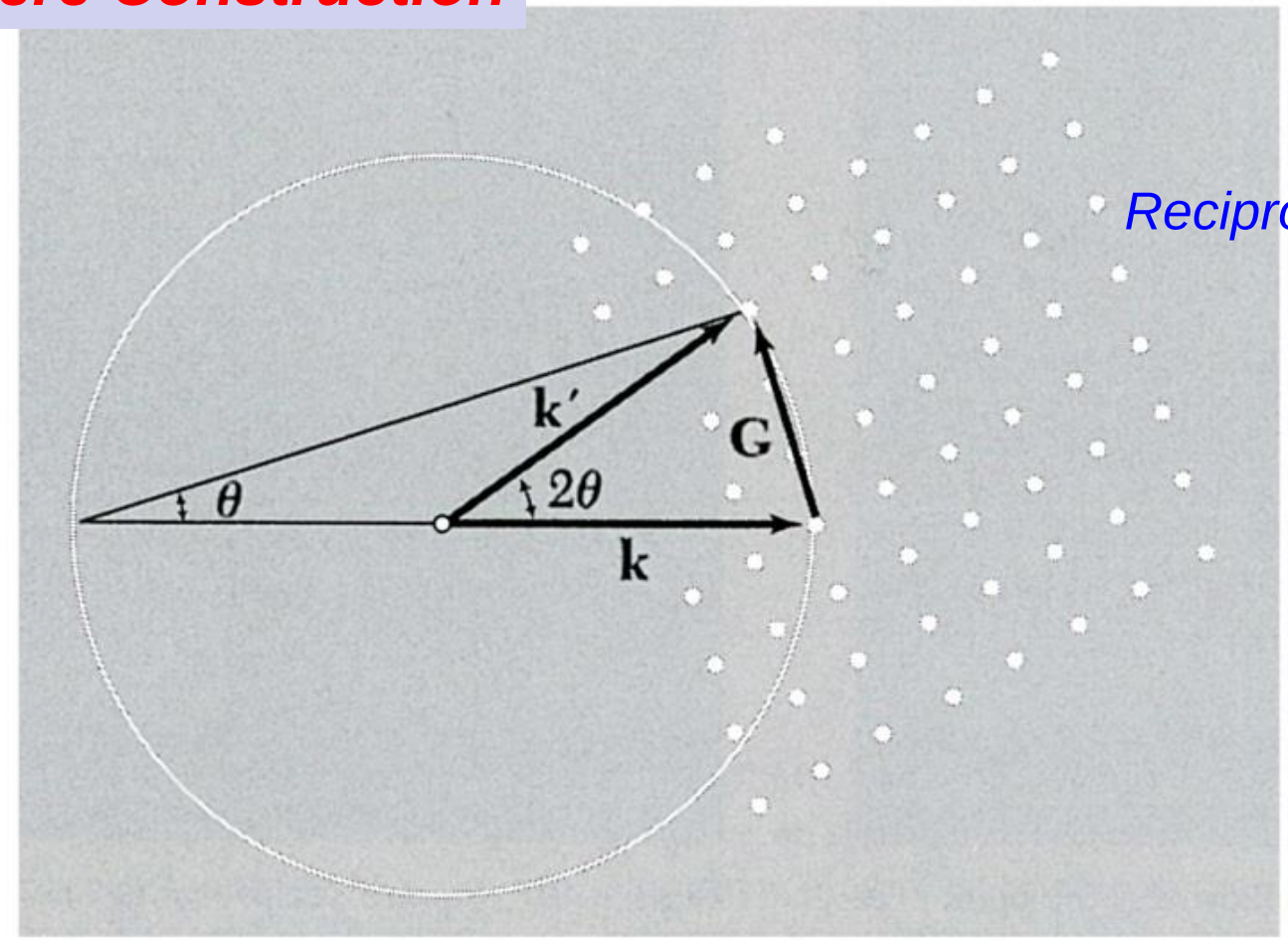
Take the scalar product of both $\Delta\mathbf{k}$ and $\mathbf{G}$ successively with $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$. From (14) and (15) we get

$$\mathbf{a}_1 \cdot \Delta\mathbf{k} = 2\pi v_1 \ ; \qquad \mathbf{a}_2 \cdot \Delta\mathbf{k} = 2\pi v_2 \ ; \qquad \mathbf{a}_3 \cdot \Delta\mathbf{k} = 2\pi v_3 \ . \tag{25}$$

These equations have a simple geometrical interpretation. The first equation $\mathbf{a}_1 \cdot \Delta\mathbf{k} = 2\pi v_1$ tells us that $\Delta\mathbf{k}$ lies on a certain cone about the direction of $\mathbf{a}_1$. The second equation tells us that $\Delta\mathbf{k}$ lies on a cone about $\mathbf{a}_2$ as well, and the third equation requires that $\Delta\mathbf{k}$ lies on a cone about $\mathbf{a}_3$.

Thus, at a reflection $\Delta\mathbf{k}$ must satisfy all three equations; it must lie at the common line of intersection of *three* cones, which is a severe condition that can be satisfied only by systematic sweeping or searching in wavelength or crystal orientation—or by sheer accident.

Ewald Sphere Construction



Reciprocal lattice

Figure 8 The points on the right-hand side are reciprocal-lattice points of the crystal. The vector **k** is drawn in the direction of the incident x-ray beam, and the origin is chosen such that **k** terminates at any reciprocal lattice point. We draw a sphere of radius $k = 2\pi/\lambda$ about the origin of **k**. A diffracted beam will be formed if this sphere intersects any other point in the reciprocal lattice. The sphere as drawn intercepts a point connected with the end of **k** by a reciprocal lattice vector **G**. The diffracted x-ray beam is in the direction $\mathbf{k}' = \mathbf{k} + \mathbf{G}$. The angle θ is the Bragg angle of Fig. 2. This construction is due to P. P. Ewald.

BRILLOUIN ZONES

A Brillouin zone is defined as a Wigner-Seitz primitive cell in the reciprocal lattice.

Take (23) divided by 4 at both sides

$$\mathbf{k} \cdot \left(\tfrac{1}{2}\mathbf{G}\right) = \left(\tfrac{1}{2}G\right)^2 \qquad (26)$$

We now work in reciprocal space, the space of the **k**'s and **G**'s. Select a vector **G** from the origin to a reciprocal lattice point. Construct a plane normal to this vector **G** at its midpoint. This plane forms a part of a zone boundary (Fig. 9a). An x-ray beam in the crystal will be diffracted if its wavevector **k** has the magnitude and direction required by (26). The diffracted beam will then be in the direction $\mathbf{k} - \mathbf{G}$, as we see from (19) with $\Delta\mathbf{k} = -\mathbf{G}$. Thus the Brillouin construction exhibits all the wavevectors **k** which can be Bragg-reflected by the crystal.

Plane1 Plane 2

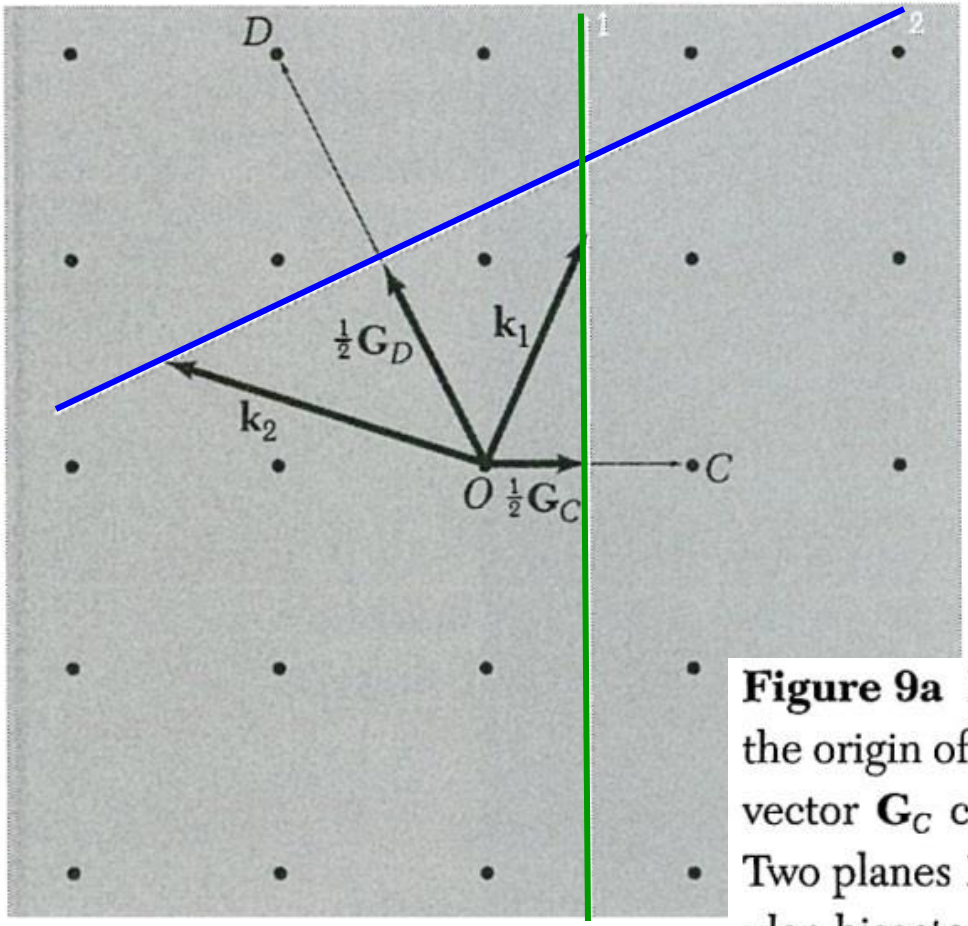


Figure 9a Reciprocal lattice points near the point O at the origin of the reciprocal lattice. The reciprocal lattice vector $\mathbf{G}_C$ connects points OC; and $\mathbf{G}_D$ connects OD. Two planes 1 and 2 are drawn which are the perpendicular bisectors of $\mathbf{G}_C$ and $\mathbf{G}_D$, respectively. Any vector from the origin to the plane 1, such as $\mathbf{k}_1$, will satisfy the diffraction condition $\mathbf{k}_1 \cdot (\frac{1}{2}\mathbf{G}_C) = (\frac{1}{2}\mathbf{G}_C)^2$. Any vector from the origin to the plane 2, such as $\mathbf{k}_2$, will satisfy the diffraction condition $\mathbf{k}_2 \cdot (\frac{1}{2}\mathbf{G}_D) = (\frac{1}{2}\mathbf{G}_D)^2$.

The set of planes that are the perpendicular bisectors of the reciprocal lattice vectors is of general importance in the theory of wave propagation in crystals. A wave whose wavevector drawn from the origin terminates on any of these planes will satisfy the condition for diffraction.

These planes divide the Fourier space of the crystal into fragments, as shown in Fig. 9b for a square lattice. The central square is a primitive cell of the reciprocal lattice. It is a **Wigner-Seitz cell** of the reciprocal lattice.

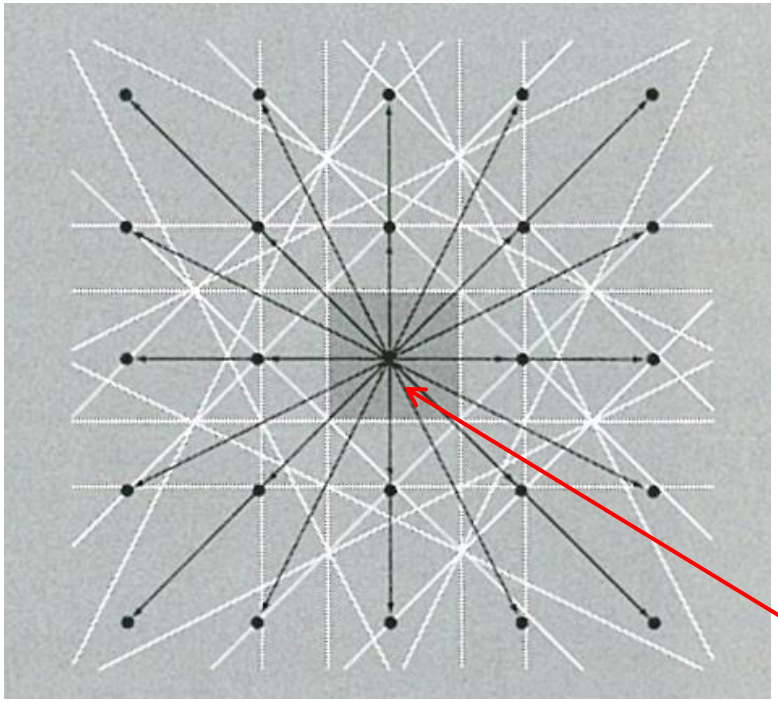


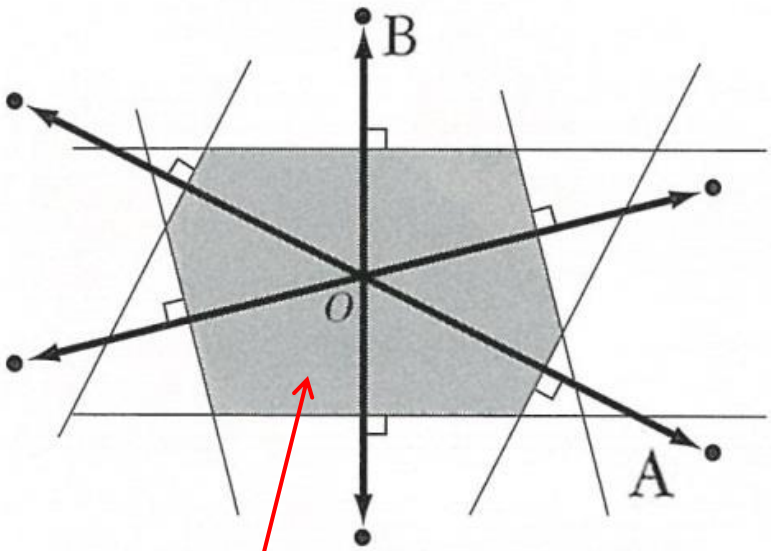
Figure 9b Square reciprocal lattice with reciprocal lattice vectors shown as fine black lines. The lines shown in white are perpendicular bisectors of the reciprocal lattice vectors. The central square is the smallest volume about the origin which is bounded entirely by white lines. The square is the Wigner-Seitz primitive cell of the reciprocal lattice. It is called the first Brillouin zone.

First Brillouin zone

The central cell in the reciprocal lattice is of special importance in the theory of solids, and we call it the first Brillouin zone. *The first Brillouin zone is the smallest volume entirely enclosed by planes that are the perpendicular bisectors of the reciprocal lattice vectors drawn from the origin.*

The first Brillouin zone of an ***oblique*** lattice in two dimensions is constructed in Fig. 10, and of a ***linear*** lattice in one dimension in Fig. 11. The zone boundaries of the linear lattice are at $\boldsymbol{k} = \pm\pi/\boldsymbol{a}$, where $\boldsymbol{a}$ is the primitive axis of the crystal lattice.

Historically, Brillouin zones are not part of the language of x-ray diffraction analysis of crystal structures, but the zones are an essential part of the analysis of the electronic energy-band structure of crystals.



First Brillouin zone

Figure 10 Construction of the first Brillouin zone for an oblique lattice in two dimensions. We first draw a number of vectors from O to nearby points in the reciprocal lattice. Next we construct lines perpendicular to these vectors at their midpoints. The smallest enclosed area is the first Brillouin zone.

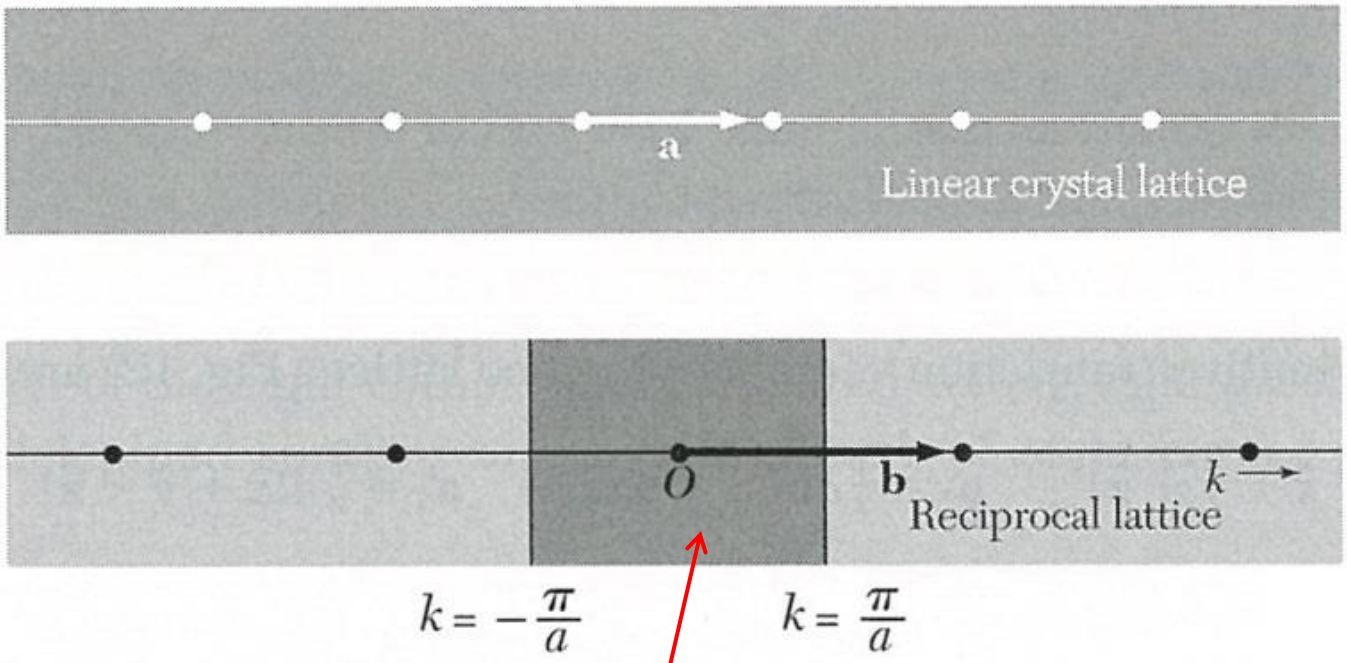


Figure 11 Crystal and reciprocal lattices in one dimension. The basis vector in the reciprocal lattice is **b**, of length equal to $2\pi/a$. The shortest reciprocal lattice vectors from the origin are **b** and $-\mathbf{b}$. The perpendicular bisectors of these vectors form the boundaries of the first Brillouin zone. The boundaries are at $k = \pm\pi/a$.

First Brillouin zone