Reciprocal Lattice to sc Lattice

The primitive translation vectors of a simple cubic lattice may be taken as the set

$$\mathbf{a}_1 = a\hat{\mathbf{x}} \; ; \qquad \mathbf{a}_2 = a\hat{\mathbf{y}} \; ; \qquad \mathbf{a}_3 = a\hat{\mathbf{z}} \; . \tag{27a}$$

Here $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, $\hat{\mathbf{z}}$ are orthogonal vectors of unit length. The volume of the cell is $\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3 = a^3$. The primitive translation vectors of the reciprocal lattice are found from the standard prescription (13):

$$\mathbf{b}_1 = (2\pi/a)\hat{\mathbf{x}} \; ; \qquad \mathbf{b}_2 = (2\pi/a)\hat{\mathbf{y}} \; ; \qquad \mathbf{b}_3 = (2\pi/a)\hat{\mathbf{z}} \; . \tag{27b}$$

Here the reciprocal lattice is itself a simple cubic lattice, now of lattice constant $2\pi/a$.

The boundaries of the first Brillouin zones are the planes normal to the six reciprocal lattice vectors $\pm\mathbf{b}_1$, $\pm\mathbf{b}_2$, $\pm\mathbf{b}_3$ at their midpoints:

$$\pm\tfrac{1}{2}\mathbf{b}_1 = \pm(\pi/a)\hat{\mathbf{x}} \; ; \qquad \pm\tfrac{1}{2}\mathbf{b}_2 = \pm(\pi/a)\hat{\mathbf{y}} \; ; \qquad \pm\tfrac{1}{2}\mathbf{b}_3 = \pm(\pi/a)\hat{\mathbf{z}} \; .$$

The six planes bound a cube of edge $2\pi/a$ and of volume $(2\pi/a)^3$; this cube is the first Brillouin zone of the sc crystal lattice.

Reciprocal Lattice to bcc Lattice

The primitive translation vectors of the bcc lattice (Fig. 12) are

$$\mathbf{a}_1 = \tfrac{1}{2}a(-\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}) \ ; \qquad \mathbf{a}_2 = \tfrac{1}{2}a(\hat{\mathbf{x}} - \hat{\mathbf{y}} + \hat{\mathbf{z}}) \ ; \qquad \mathbf{a}_3 = \tfrac{1}{2}a(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}}) \ , \tag{28}$$

where a is the side of the conventional cube and $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, $\hat{\mathbf{z}}$ are orthogonal unit vectors parallel to the cube edges. The volume of the primitive cell is

$$V = |\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3| = \tfrac{1}{2}a^3 \ . \tag{29}$$

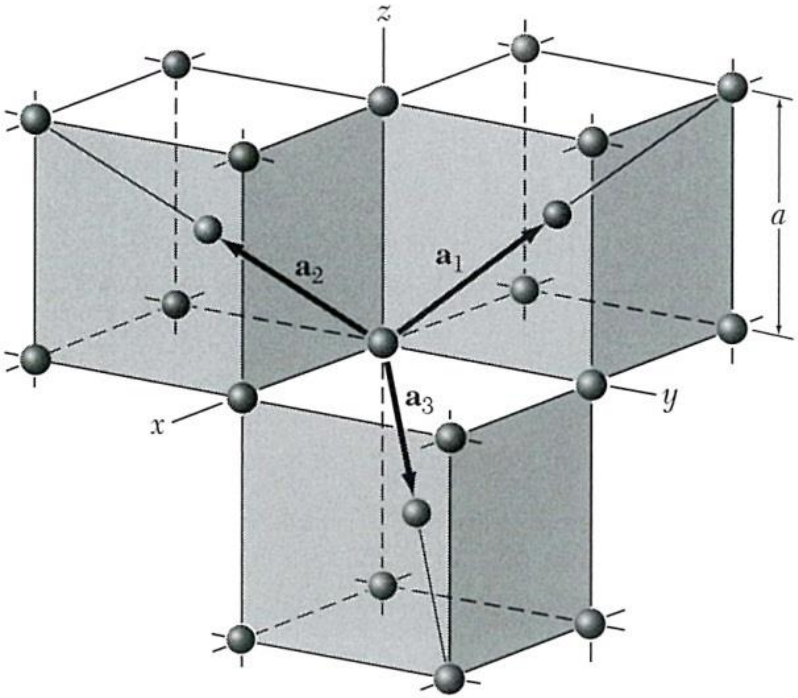


Figure 12 Primitive basis vectors of the body-centered cubic lattice.

The primitive translations of the reciprocal lattice are defined by (13). We have, using (28),

$$\mathbf{b}_1 = (2\pi/a)(\hat{\mathbf{y}} + \hat{\mathbf{z}}) \ ; \qquad \mathbf{b}_2 = (2\pi/a)(\hat{\mathbf{x}} + \hat{\mathbf{z}}) \ ; \qquad \mathbf{b}_3 = (2\pi/a)(\hat{\mathbf{x}} + \hat{\mathbf{y}}) \ . \qquad (30)$$

Note by comparison with Fig. 14 (p. 42) that these are just the primitive vectors of an fcc lattice, so that an fcc lattice is the reciprocal lattice of the bcc lattice.

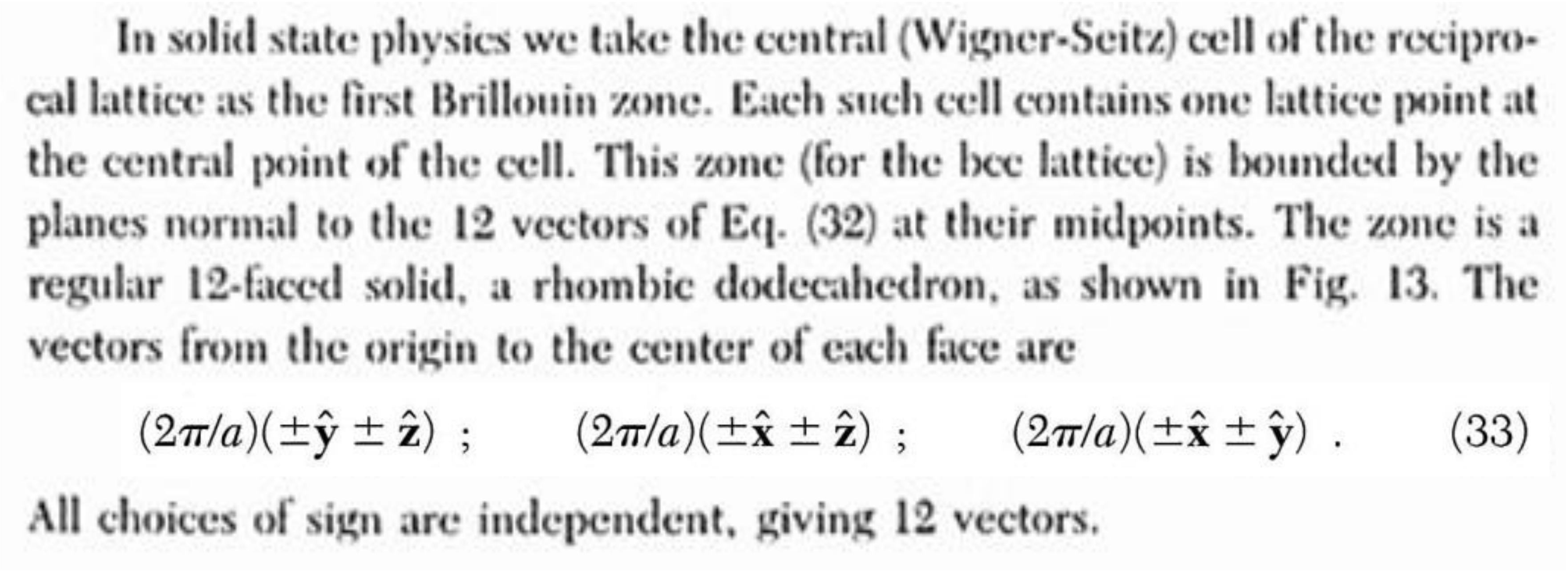
The general reciprocal lattice vector is, for integral v_1, v_2, v_3,

$$\mathbf{G} = v_1\mathbf{b}_1 + v_2\mathbf{b}_2 + v_3\mathbf{b}_3 = (2\pi/\mathrm{a})[(v_2 + v_3)\hat{\mathbf{x}} + (v_1 + v_3)\hat{\mathbf{y}} + (v_1 + v_2)\hat{\mathbf{z}}] \ . \qquad (31)$$

The shortest G's are the following 12 vectors, where all choices of sign are independent:

$$(2\pi/a)(\pm\hat{\mathbf{y}} \pm \hat{\mathbf{z}}) \ ; \qquad (2\pi/a)(\pm\hat{\mathbf{x}} \pm \hat{\mathbf{z}}) \ ; \qquad (2\pi/a)(\pm\hat{\mathbf{x}} \pm \hat{\mathbf{y}}) \ . \qquad (32)$$

The primitive cell of the reciprocal lattice is the parallelepiped described by the $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$ defined by (30). The volume of this cell in reciprocal space is $\mathbf{b}_1 \cdot \mathbf{b}_2 \times \mathbf{b}_3 = 2(2\pi/a)^3$. The cell contains one reciprocal lattice point, because each of the eight corner points is shared among eight parallelepipeds. Each parallelepiped contains one-eighth of each of eight corner points.

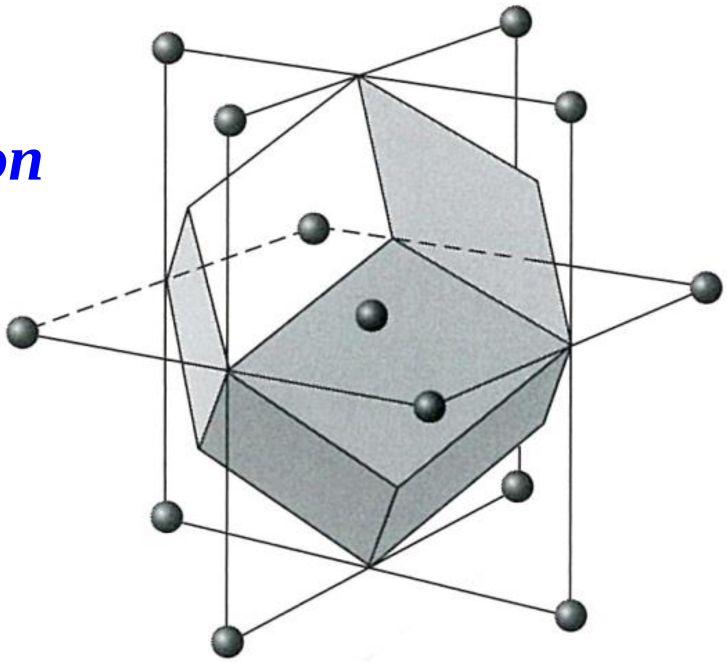


In solid state physics we take the central (Wigner-Seitz) cell of the reciprocal lattice as the first Brillouin zone. Each such cell contains one lattice point at the central point of the cell. This zone (for the bcc lattice) is bounded by the planes normal to the 12 vectors of Eq. (32) at their midpoints. The zone is a regular 12-faced solid, a rhombic dodecahedron, as shown in Fig. 13. The vectors from the origin to the center of each face are

$$(2\pi/a)(\pm\hat{\mathbf{y}} \pm \hat{\mathbf{z}}) \ ; \qquad (2\pi/a)(\pm\hat{\mathbf{x}} \pm \hat{\mathbf{z}}) \ ; \qquad (2\pi/a)(\pm\hat{\mathbf{x}} \pm \hat{\mathbf{y}}) \ . \qquad (33)$$

All choices of sign are independent, giving 12 vectors.

Rhombic dodecahedron



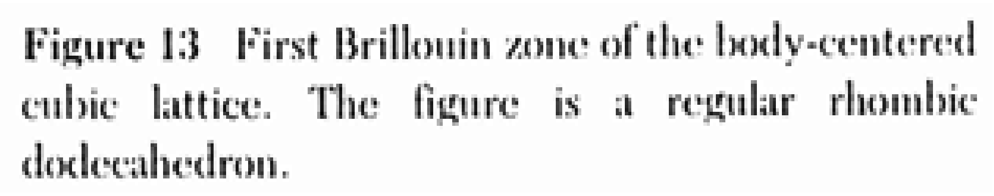
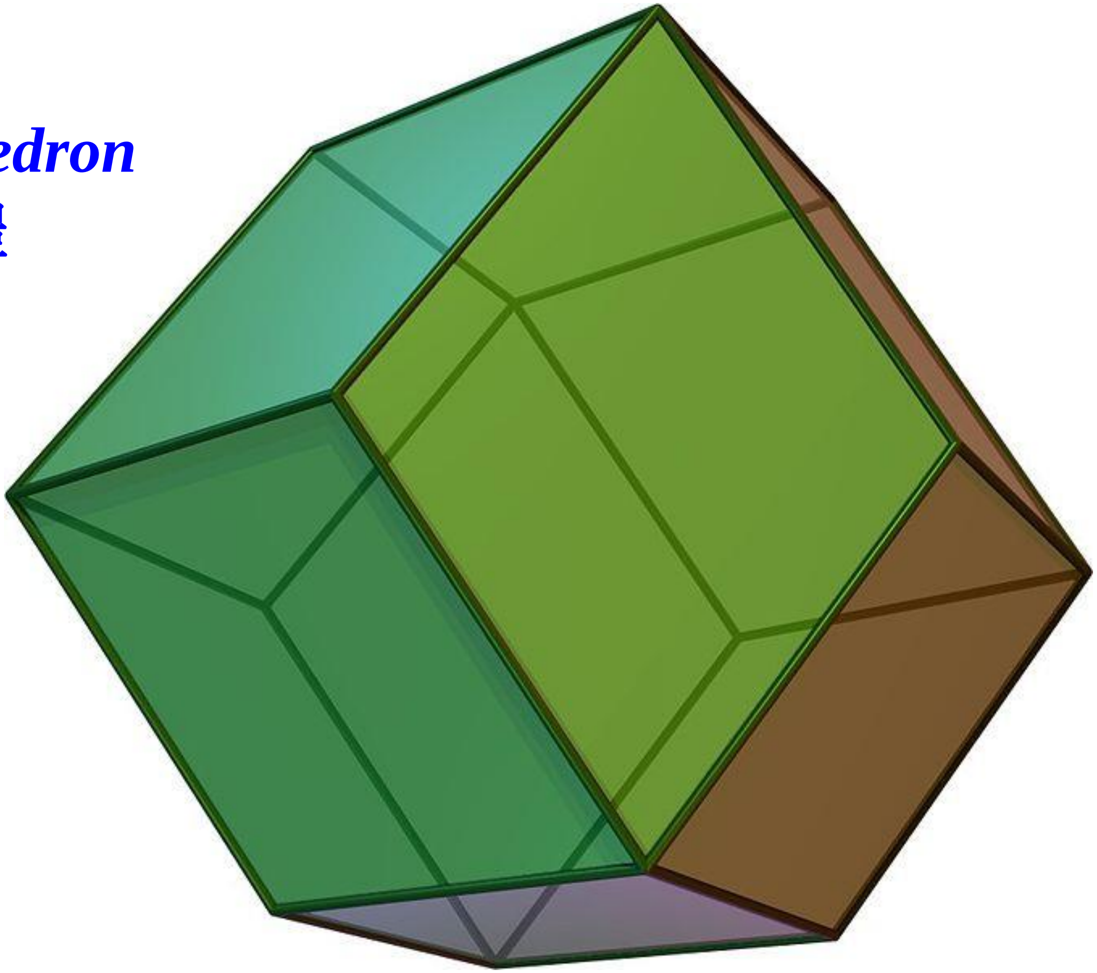


Figure 13 First Brillouin zone of the body-centered cubic lattice. The figure is a regular rhombic dodecahedron.

Rhombic Dodecahedron

菱形 十二面體



The long diagonal of each face is exactly √2 times the length of the short diagonal, so that the acute angles on each face measure arc Cos(1/3), or approximately 70.53°

Reciprocal Lattice to fcc Lattice

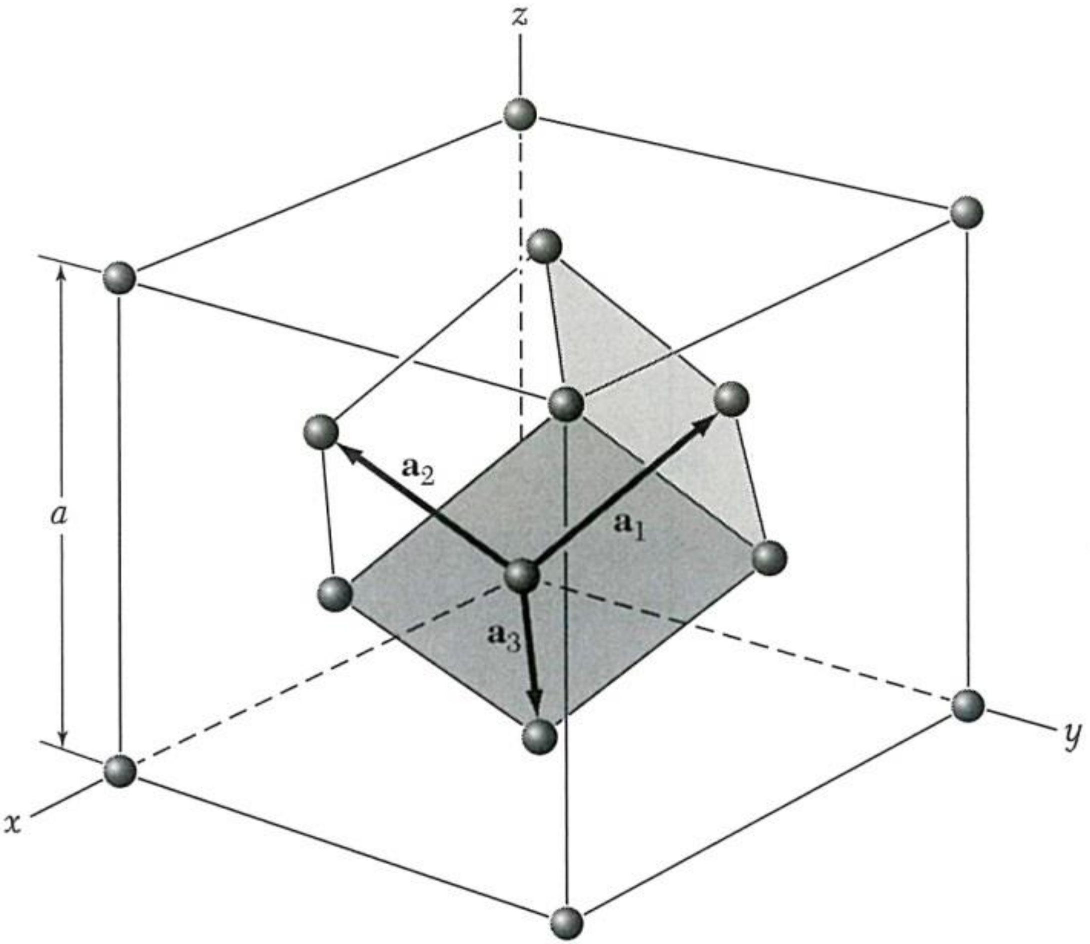


Figure 14 Primitive basis vectors of the face-centered cubic lattice.

Reciprocal Lattice to fcc Lattice

The primitive translation vectors of the fcc lattice of Fig. 14 are

$$\mathbf{a}_1 = \frac{1}{2}a(\hat{\mathbf{y}} + \hat{\mathbf{z}})\ ; \quad \mathbf{a}_2 = \frac{1}{2}a(\hat{\mathbf{x}} + \hat{\mathbf{z}})\ ; \quad \mathbf{a}_3 = \frac{1}{2}a(\hat{\mathbf{x}} + \hat{\mathbf{y}})\ . \tag{34}$$

The volume of the primitive cell is

$$V = |\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3| = \frac{1}{4}a^3 \tag{35}$$

The primitive translation vectors of the lattice reciprocal to the fcc lattice are

$$\begin{gathered} \mathbf{b}_1 = (2\pi/a)(-\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})\ ; \qquad \mathbf{b}_2 = (2\pi/a)(\hat{\mathbf{x}} - \hat{\mathbf{y}} + \hat{\mathbf{z}})\ ; \\ \mathbf{b}_3 = (2\pi/a)(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}})\ . \end{gathered} \tag{36}$$

These are primitive translation vectors of a bcc lattice, so that the bcc lattice is reciprocal to the fcc lattice. The volume of the primitive cell of the reciprocal lattice is $4(2\pi/a)^3$.

The shortest **G**'s are the eight vectors:

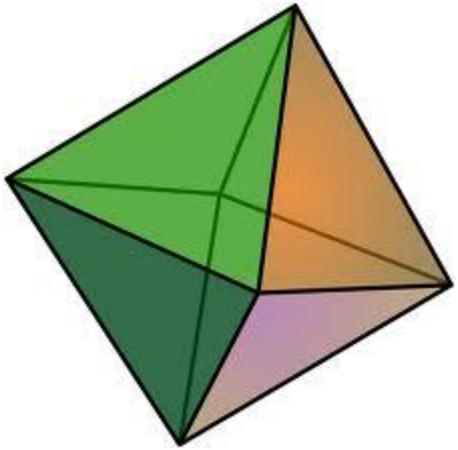
$$(2\pi/a)(\pm\hat{\mathbf{x}} \pm \hat{\mathbf{y}} \pm \hat{\mathbf{z}}) \ . \tag{37}$$

The boundaries of the central cell in the reciprocal lattice are determined for the most part by the eight planes normal to these vectors at their midpoints. But the corners of the octahedron thus formed are cut by the planes that are the perpendicular bisectors of six other reciprocal lattice vectors:

$$(2\pi/a)(\pm 2\hat{\mathbf{x}}) \ ; \qquad (2\pi/a)(\pm 2\hat{\mathbf{y}}) \ ; \qquad (2\pi/a)(\pm 2\hat{\mathbf{z}}) \ . \tag{38}$$

Note that $(2\pi/a)(2\hat{\mathbf{x}})$ is a reciprocal lattice vector because it is equal to $\mathbf{b}_2 + \mathbf{b}_3$. The first Brillouin zone is the smallest bounded volume about the origin, the truncated octahedron shown in Fig. 15. The six planes bound a cube of edge $4\pi/a$ and (before truncation) of volume $(4\pi/a)^3$.

Octahedron



Truncated Octahedron

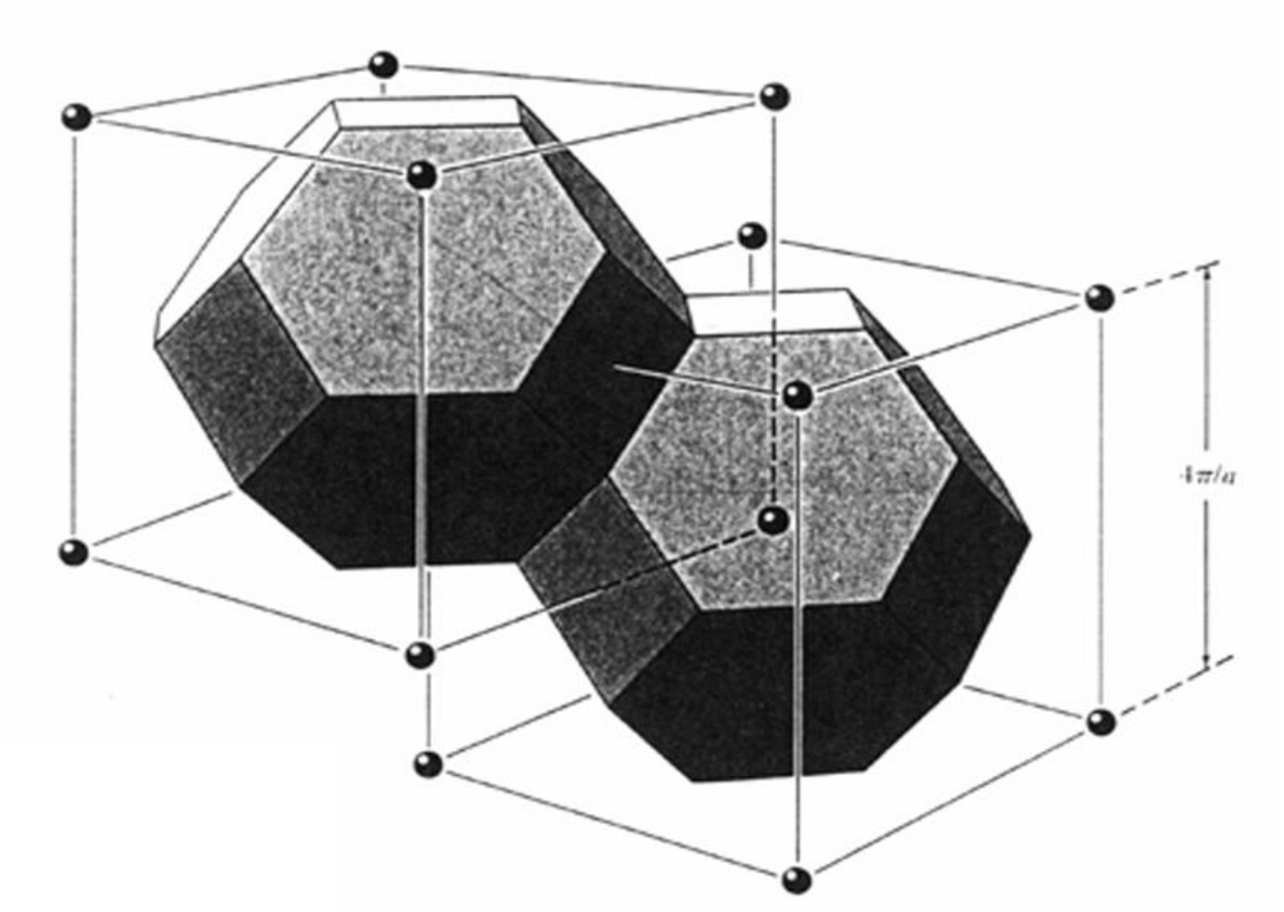


Figure 15 Brillouin zones of the face-centered cubic lattice. The cells are in reciprocal space, and the reciprocal lattice is body centered.

FOURIER ANALYSIS OF THE BASIS

When the diffraction condition $\Delta\mathbf{k} = \mathbf{G}$ of Eq. (21) is satisfied, the scattering amplitude is determined by (18), which for a crystal of N cells may be written as

$$F_G = N \int_{cell} dV\, n(\mathbf{r}) \exp(-i\mathbf{G} \cdot \mathbf{r}) = NS_G \tag{39}$$

The quantity S_G is called the **structure factor** and is defined as an integral over a single cell, with $\mathbf{r} = 0$ at one corner.

Often it is useful to write the electron concentration $n(\mathbf{r})$ as the superposition of electron concentration functions n_j associated with each atom j of the cell. If $\mathbf{r}_j$ is the vector to the center of atom j, then the function $n_j(\mathbf{r} - \mathbf{r}_j)$ defines the contribution of that atom to the electron concentration at $\mathbf{r}$. The total electron concentration at $\mathbf{r}$ due to all atoms in the cell is the sum

$$n(\mathbf{r}) = \sum_{j=1}^{s} n_j(\mathbf{r} - \mathbf{r}_j) \tag{40}$$

over the s atoms of the basis. The decomposition of $n(\mathbf{r})$ is not unique, for we cannot always say how much charge is associated with each atom. This is not an important difficulty.

The structure factor defined by (39) may now be written as integrals over the s atoms of a cell:

$$S_{\mathbf{G}} = \sum_j \int dV\, n_j(\mathbf{r} - \mathbf{r}_j) \exp(-i\mathbf{G}\cdot\mathbf{r}) = \sum_j \exp(-i\mathbf{G}\cdot\mathbf{r}_j) \int dV\, n_j(\boldsymbol{\rho}) \exp(-i\mathbf{G}\cdot\boldsymbol{\rho}) \ , \tag{41}$$

where $\underline{\boldsymbol{\rho} \equiv \mathbf{r} - \mathbf{r}_j}$.

We now define the atomic form factor as

$$f_j = \int dV\, n_j(\boldsymbol{\rho}) \exp(-i\mathbf{G}\cdot\boldsymbol{\rho}) \ , \tag{42}$$

integrated over all space. If $n_j(\boldsymbol{\rho})$ is an atomic property, f_j is an atomic property.

We combine (41) and (42) to obtain the structure factor of the basis in the form

$$\boxed{S_{\mathbf{G}} = \sum_j f_j \exp(-i\mathbf{G}\cdot\mathbf{r}_j) \ .} \tag{43}$$

The usual form of this result follows on writing for atom j:

$$\mathbf{r}_j = x_j\mathbf{a}_1 + y_j\mathbf{a}_2 + z_j\mathbf{a}_3 \ , \tag{44}$$

as in (1.4). Then, for the reflection labelled by v_1, v_2, v_3 we have

$$\begin{aligned}\mathbf{G}\cdot\mathbf{r}_j &= (v_1\mathbf{b}_1 + v_2\mathbf{b}_2 + v_3\mathbf{b}_3)\cdot(x_j\mathbf{a}_1 + y_j\mathbf{a}_2 + z_j\mathbf{a}_3) \\ &= 2\pi(v_1x_j + v_2y_j + v_3z_j) \ ,\end{aligned} \tag{45}$$

so that (43) becomes

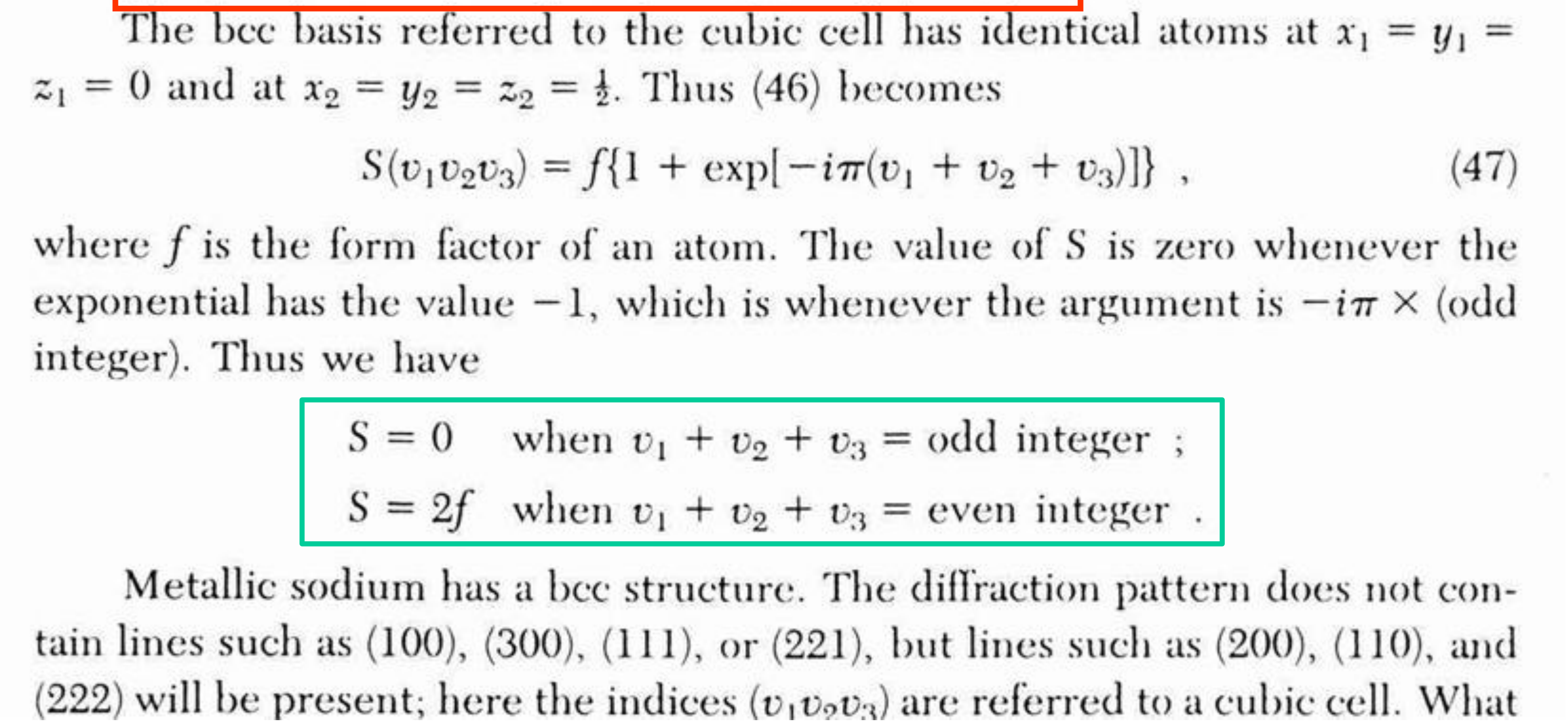
$$\boxed{S_{\mathbf{G}}(v_1v_2v_3) = \sum_j f_j \exp[-i2\pi(v_1x_j + v_2y_j + v_3z_j)] \ .} \tag{46}$$

The structure factor S need not be real because the scattered intensity will involve S^*S, where S^* is the complex conjugate of S so that S^*S is real.

At a zero of $S_{\mathbf{G}}$ the scattered intensity will be zero, even though $\mathbf{G}$ is a perfectly good reciprocal lattice vector. What happens if we choose the cell in another way, as a conventional cell instead of a primitive cell, for example? The basis is changed, but in such a way that the physical scattering is unchanged. Thus for two choices, 1 and 2, it is not hard to satisfy yourself from (39) that

$$N_1(\text{cell}) \times S_1(\text{basis}) = N_2(\text{cell}) \times S_2(\text{basis}) \ .$$

Structural Factor of the bcc Lattice



The bcc basis referred to the cubic cell has identical atoms at $x_1 = y_1 = z_1 = 0$ and at $x_2 = y_2 = z_2 = \frac{1}{2}$. Thus (46) becomes

$$S(v_1v_2v_3) = f\{1 + \exp[-i\pi(v_1 + v_2 + v_3)]\} \ , \tag{47}$$

where f is the form factor of an atom. The value of S is zero whenever the exponential has the value -1, which is whenever the argument is $-i\pi \times$ (odd integer). Thus we have

$$\boxed{\begin{aligned} S &= 0 \quad \text{when } v_1 + v_2 + v_3 = \text{odd integer} \ ; \\ S &= 2f \quad \text{when } v_1 + v_2 + v_3 = \text{even integer} \ . \end{aligned}}$$

Metallic sodium has a bcc structure. The diffraction pattern does not contain lines such as (100), (300), (111), or (221), but lines such as (200), (110), and (222) will be present; here the indices $(v_1v_2v_3)$ are referred to a cubic cell. What

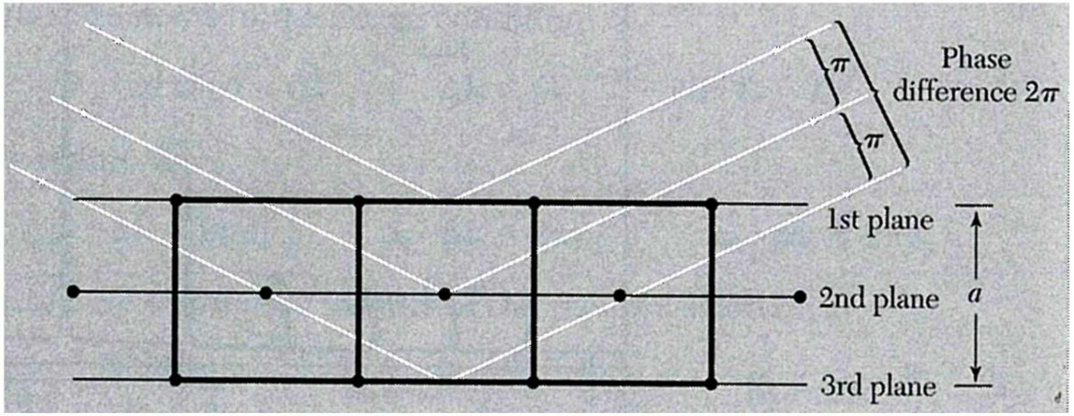


Figure 16 Explanation of the absence of a (100) reflection from a body-centered cubic lattice. The phase difference between successive planes is π, so that the reflected amplitude from two adjacent planes is $1 + e^{-i\pi} = 1 - 1 = 0$.

Structure Factor of the fcc Lattice

The basis of the fcc structure referred to the cubic cell has identical atoms at 000; $0\frac{1}{2}\frac{1}{2}$; $\frac{1}{2}0\frac{1}{2}$; $\frac{1}{2}\frac{1}{2}0$. Thus (46) becomes

$$S(v_1v_2v_3) = f\{1 + \exp[-i\pi(v_2 + v_3)] + \exp[-i\pi(v_1 + v_3)] + \exp[-i\pi(v_1 + v_2)]\} \;. \tag{48}$$

If all indices are even integers, $S = 4f$; similarly if all indices are odd integers. But if only one of the integers is even, two of the exponents will be odd multiples of $-i\pi$ and S will vanish. If only one of the integers is odd, the same argument applies and S will also vanish.

Thus in the fcc lattice no reflections can occur for which the indices are partly even and partly odd.

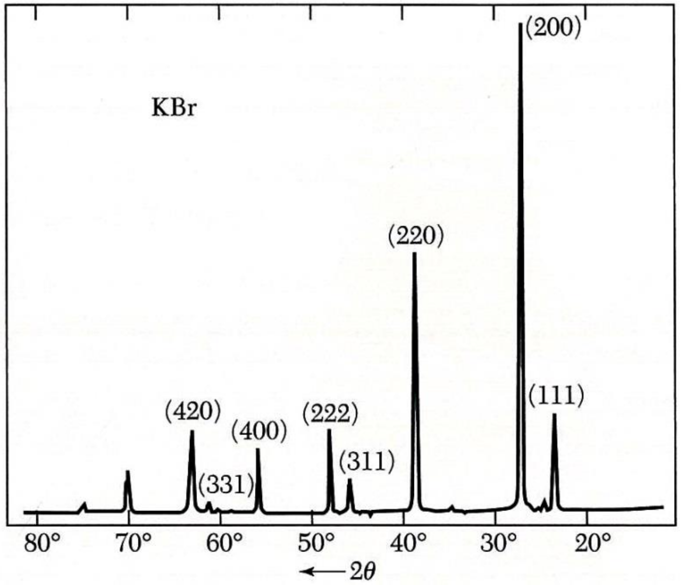


Figure 17 Comparison of x-ray reflections from KCl and KBr powders. In KCl the numbers of electrons of K^+ and Cl^- ions are equal. The scattering amplitudes $f(K^+)$ and $f(Cl^-)$ are almost exactly equal, so that the crystal looks to x-rays as if it were a monatomic simple cubic lattice of lattice constant $a/2$. Only even integers occur in the reflection indices when these are based on a cubic lattice of lattice constant a. In KBr the form factor of Br^- is quite different than that of K^+, and all reflections of the fcc lattice are present. (Courtesy of R. van Nordstrand.)

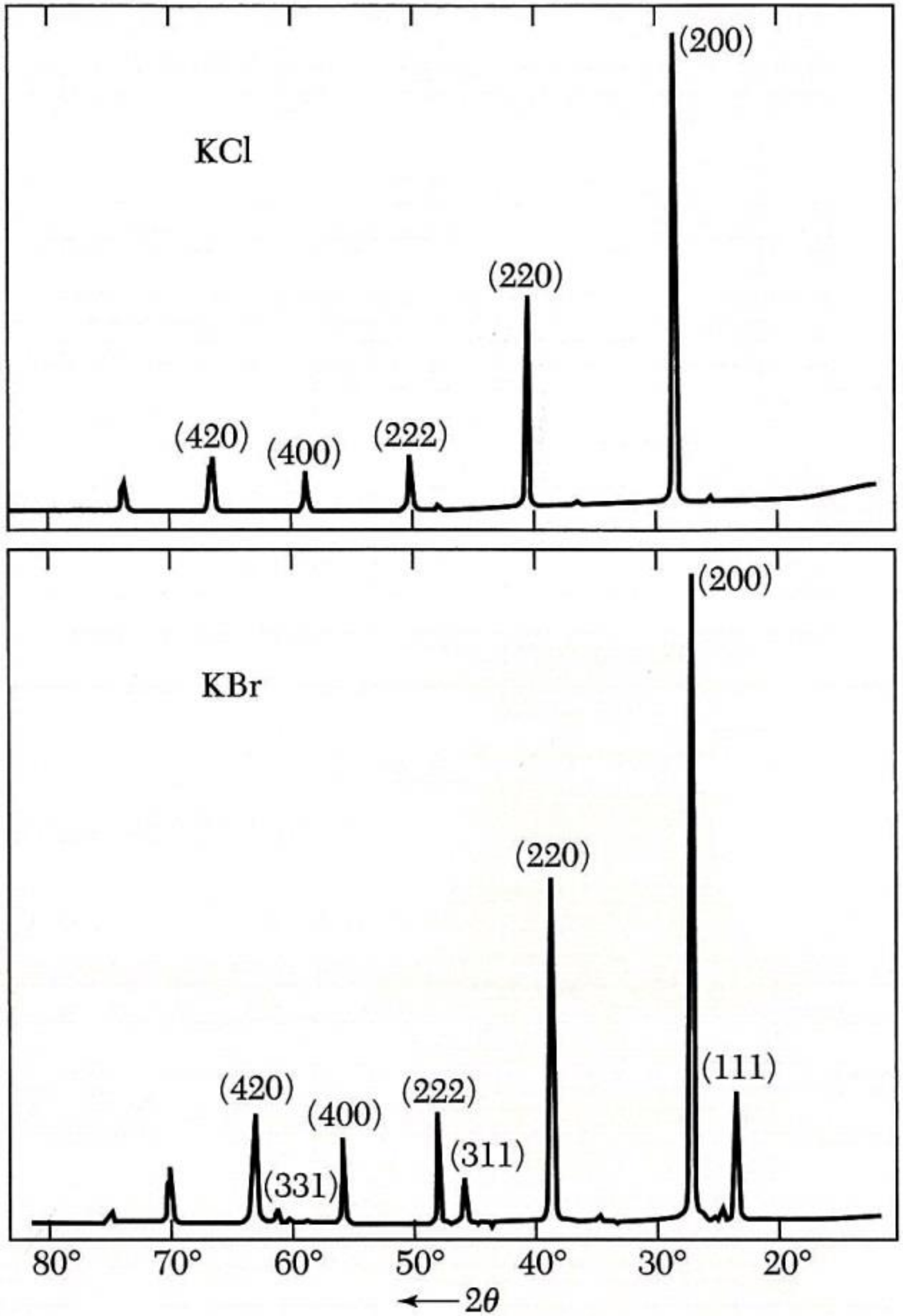


Figure 17 Comparison of x-ray reflections from KCl and KBr powders. In KCl the numbers of electrons of K^+ and Cl^- ions are equal. The scattering amplitudes $f(K^+)$ and $f(Cl^-)$ are almost exactly equal, so that the crystal looks to x-rays as if it were a monatomic simple cubic lattice of lattice constant $a/2$. Only even integers occur in the reflection indices when these are based on a cubic lattice of lattice constant a. In KBr the form factor of Br^- is quite different than that of K^+, and all reflections of the fcc lattice are present. (Courtesy of R. van Nordstrand.)

Atomic Form Factor

In the expression (46) for the structure factor, there occurs the quantity f_j, which is a measure of the scattering power of the jth atom in the unit cell. The value of f involves the number and distribution of atomic electrons, and the wavelength and angle of scattering of the radiation. We now give a classical calculation of the scattering factor.

The scattered radiation from a single atom takes account of interference effects within the atom. We defined the form factor in (42):

$$f_j = \int dV\, n_j(\mathbf{r}) \exp(-i\mathbf{G}\cdot\mathbf{r}) \ , \tag{49}$$

with the integral extended over the electron concentration associated with a single atom. Let $\mathbf{r}$ make an angle α with $\mathbf{G}$; then $\mathbf{G}\cdot\mathbf{r} = Gr\cos\alpha$. If the electron distribution is spherically symmetric about the origin, then

$$\begin{aligned} f_j &= 2\pi \int dr\, r^2\, d(\cos\alpha)\, n_j(r) \exp(-iGr\cos\alpha) \\ &= 2\pi \int dr\, r^2 n_j(r) \cdot \frac{e^{iGr} - e^{-iGr}}{iGr} \ , \end{aligned}$$

after integration over $d(\cos\alpha)$ between -1 and 1. Thus the form factor is given by

$$\boxed{f_j = 4\pi \int dr\, n_j(r) r^2 \, \frac{\sin Gr}{Gr} \ .} \tag{50}$$

If the same total electron density were concentrated at $r = 0$, only $Gr = 0$ would contribute to the integrand. In this limit $(\sin Gr)/Gr = 1$, and

$$f_j = 4\pi \int dr\, n_j(r) r^2 = Z \ , \tag{51}$$

the number of atomic electrons. Therefore f is the ratio of the radiation amplitude scattered by the actual electron distribution in an atom to that scattered by one electron localized at a point.

In the forward direction $G = 0$, and f reduces again to the value Z.

The overall electron distribution in a solid as seen in x-ray diffraction is fairly close to that of the appropriate free atoms. This statement does not mean that the outermost or valence electrons are not redistributed in forming the solid; it means only that the x-ray reflection intensities are represented well by the free atom values of the form factors and are not very sensitive to small redistributions of the electrons.

End of Chapter 2

As an example, Batterman and co-workers find agreement within 1 percent in a comparison of the x-ray intensities of Bragg reflections of metallic iron, copper, and aluminum with the theoretical free atom values from wavefunction calculations. The results for aluminum are shown in Fig. 18.

There have been many attempts to obtain direct x-ray evidence about the actual electron distribution in a covalent chemical bond, particularly in crystals having the diamond structure.

Al

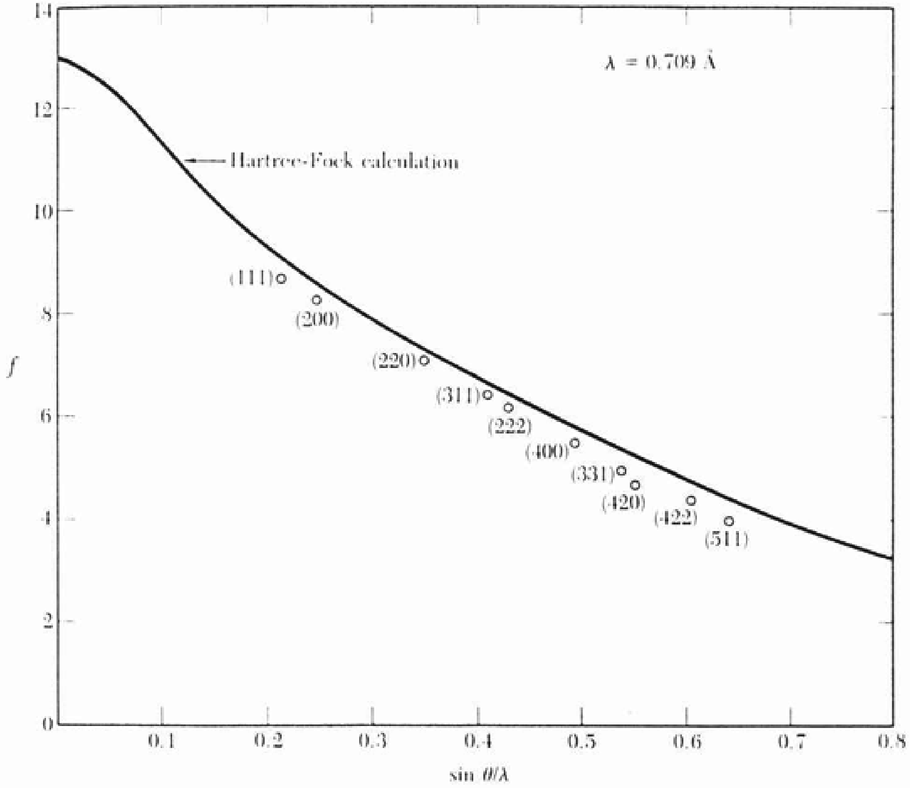


Figure 18 Absolute experimental atomic scattering factors for metallic aluminum, after Batterman, Chipman, and DeMarco. Each observed reflection is labeled. No reflections occur for indices partly even and partly odd, as predicted for an fcc crystal.

QUASICRYSTALS

$Al_{0.86}Mn_{0.14}$

In 1984 quasicrystals were first observed;[1] these are structures which cannot be indexed to any Bravais lattice and "which have symmetries intermediate between a crystal and a liquid." They were first observed in grains of size 2 μm in an alloy of Al with 14 at pct Mn. The smaller Mn atoms are each surrounded by 12 Al atoms arranged at the corners of an icosahedron. The structure is made up of parallel icosahedra attached at their edges. Crystals cannot exhibit the fivefold symmetry of an icosahedron, but a crystal can be constructed by nucleation at a center cell, followed by outward growth from there. All of the space of a nodule cannot be filled by repeating the basic unit (see Figures 19 and 1.7 for the picture in two dimensions), although the "parallel" part of the specification does give a long-range orientational order to the structure. It is perhaps surprising that the x-ray diffraction pattern of such a structure can have fivefold symmetry; that is how they were first observed.

The known quasicrystals are intermetallic alloys and are very poor electrical conductors; they are nearly insulators with a somewhat well-defined band gap (Chapter 7) at the Fermi level. They are of great interest intellectually in expanding the definition of crystal lattice.

A distinctly different crystal diffraction pattern results from an almost periodic structure, one that is neither rigorously periodic nor simply amorphous (as for a glass, Chapter 17). An almost periodic structure can be expressed in one dimension if we are given the electron charge density wave:

$$\rho(x) = \Sigma[C_n \cos[2\pi n(1 + \tau)x/a] \ , \tag{52}$$

where τ is an irrational fraction. The terms in $2\pi n/a$ by themselves give the usual lattice with translational periodicity a. When the terms in τ are added, the charge density is almost periodic; that is, the period $(1 + \tau)a$ is not an integral multiple of the period a, because τ is irrational. The period gives a long-range nonrandom order to the structure, and the long-range order gives a diffraction pattern, which appears split off from the pattern defined by the short-range order. This is dominated by the reciprocal lattice points in n_1, but will appear to be clustered and spread out (broadened). The diffraction pattern of a three-dimensional quasicrystal is quite different, however; the pattern is well defined and can have the fivefold symmetry by which quasicrystals were first discovered. A computer-generated diffraction pattern with fivefold symmetry is shown in Figure 20.

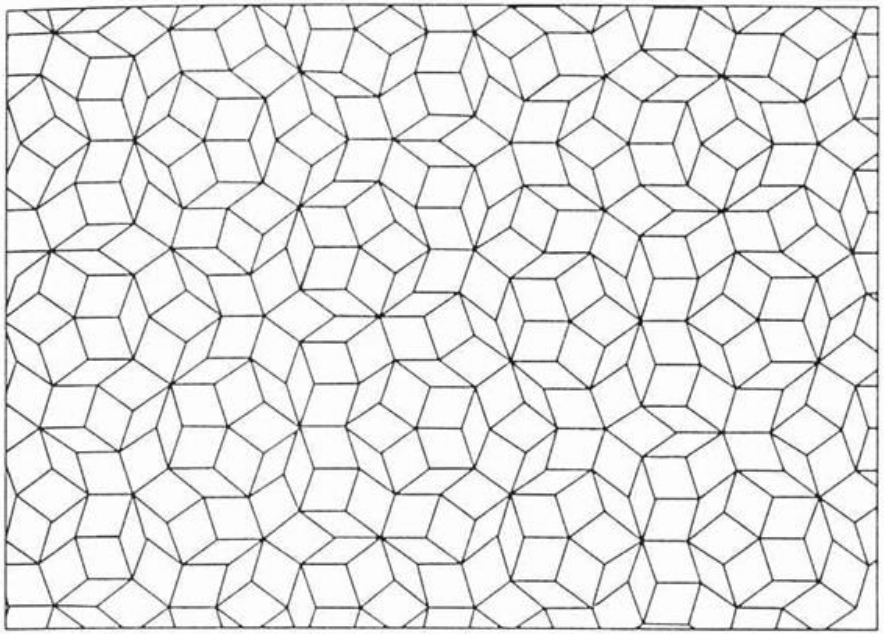


Figure 19 A quasicrystal tiling in two dimensions, after the work of Penrose. The long-range orientational order and the long-range nonperiodic order are shown.