1

Crystal Structure

UNITS: 1 Å = 1 angstrom = 10^{-8} cm = 0.1 nm = 10^{-10} m.

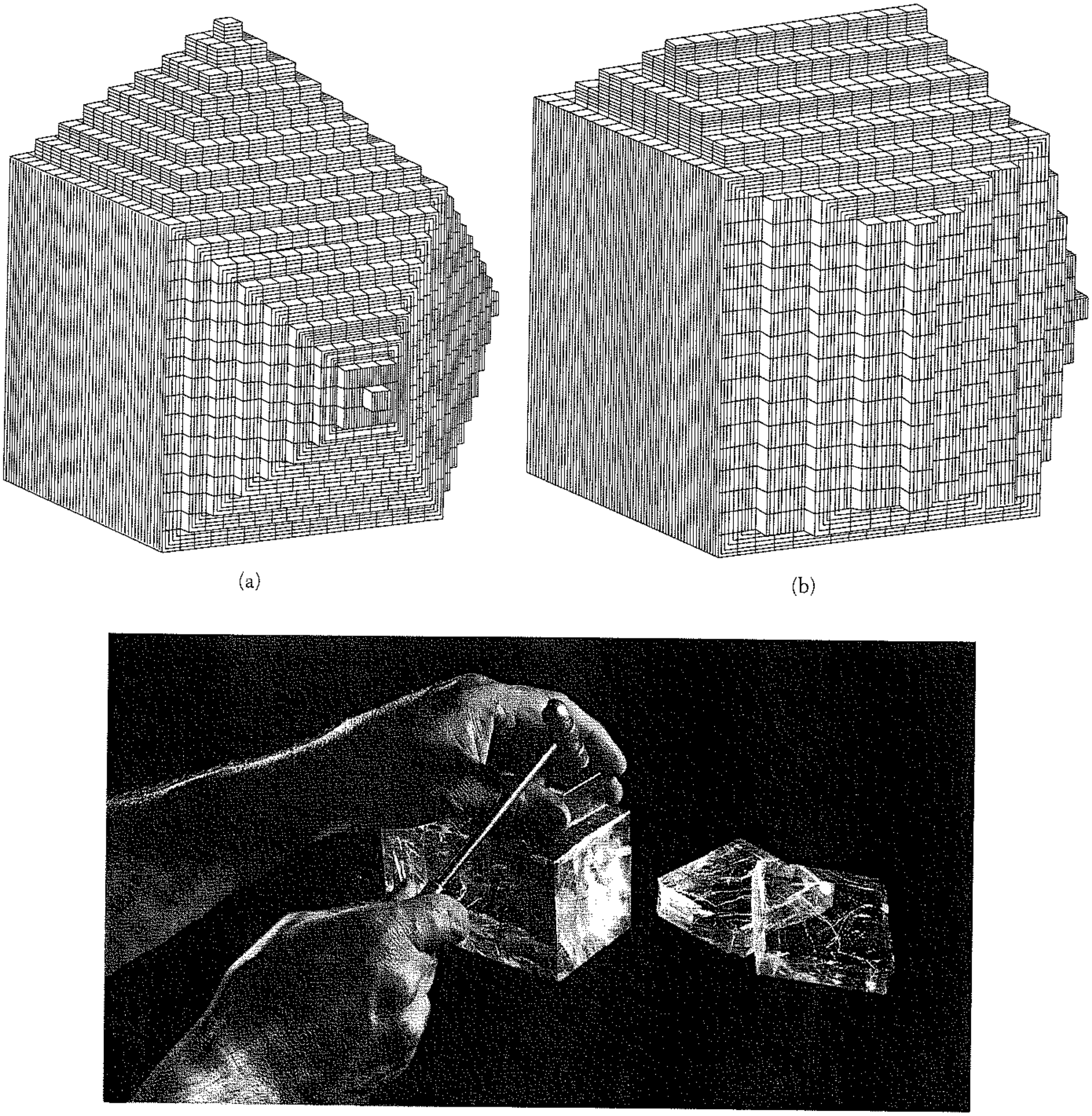

(a)
(b)
(c)

Figure 1 Relation of the external form of crystals to the form of the elementary building blocks. The building blocks are identical in (a) and (b), but different crystal faces are developed. (c) Cleaving a crystal of rocksalt.

CHAPTER 1: CRYSTAL STRUCTURE

PERIODIC ARRAYS OF ATOMS

The serious study of solid state physics began with the discovery of x-ray diffraction by crystals and the publication of a series of simple calculations of the properties of crystals and of electrons in crystals. Why crystalline solids rather than noncrystalline solids? The important electronic properties of solids are best expressed in crystals. Thus the properties of the most important semiconductors depend on the crystalline structure of the host, essentially because electrons have short wavelength components that respond dramatically to the regular periodic atomic order of the specimen. Noncrystalline materials, notably glasses, are important for optical propagation because light waves have a longer wavelength than electrons and see an average over the order, and not the less regular local order itself.

We start the book with crystals. A crystal is formed by adding atoms in a constant environment, usually in a solution. Possibly the first crystal you ever saw was a natural quartz crystal grown in a slow geological process from a silicate solution in hot water under pressure. The crystal form develops as identical building blocks are added continuously. Figure 1 shows an idealized picture of the growth process, as imagined two centuries ago. The building blocks here are atoms or groups of atoms. The crystal thus formed is a three-dimensional periodic array of identical building blocks, apart from any imperfections and impurities that may accidentally be included or built into the structure.

The original experimental evidence for the periodicity of the structure rests on the discovery by mineralogists that the index numbers that define the orientations of the faces of a crystal are exact integers. This evidence was supported by the discovery in 1912 of x-ray diffraction by crystals, when Laue developed the theory of x-ray diffraction by a periodic array, and his coworkers reported the first experimental observation of x-ray diffraction by crystals. The importance of x-rays for this task is that they are waves and have a wavelength comparable with the length of a building block of the structure. Such analysis can also be done with neutron diffraction and with electron diffraction, but x-rays are usually the tool of choice.

The diffraction work proved decisively that crystals are built of a periodic array of atoms or groups of atoms. With an established atomic model of a crystal, physicists could think much further, and the development of quantum theory was of great importance to the birth of solid state physics. Related studies have been extended to noncrystalline solids and to quantum fluids. The wider field is known as condensed matter physics and is one of the largest and most vigorous areas of physics.

Lattice Translation Vectors

An ideal crystal is constructed by the infinite repetition of identical groups of atoms (Fig. 2). A group is called the **basis**. The set of mathematical points to which the basis is attached is called the **lattice**. The lattice in three dimensions may be defined by three translation vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$, such that the arrangement of atoms in the crystal looks the same when viewed from the point $\mathbf{r}$ as when viewed from every point $\mathbf{r}'$ translated by an integral multiple of the $\mathbf{a}$'s:

$$\mathbf{r}' = \mathbf{r} + u_1\mathbf{a}_1 + u_2\mathbf{a}_2 + u_3\mathbf{a}_3 . \qquad (1)$$

Here u_1, u_2, u_3 are arbitrary integers. The set of points $\mathbf{r}'$ defined by (1) for all u_1, u_2, u_3 defines the lattice.

The lattice is said to be **primitive** if any two points from which the atomic arrangement looks the same always satisfy (1) with a suitable choice of the integers u_i. This statement defines the **primitive translation vectors** $\mathbf{a}_i$. There is no cell of smaller volume than $\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3$ that can serve as a building block for the crystal structure. We often use the primitive translation vectors to define the **crystal axes**, which form three adjacent edges of the primitive parallelepiped. Nonprimitive axes are often used as crystal axes when they have a simple relation to the symmetry of the structure.

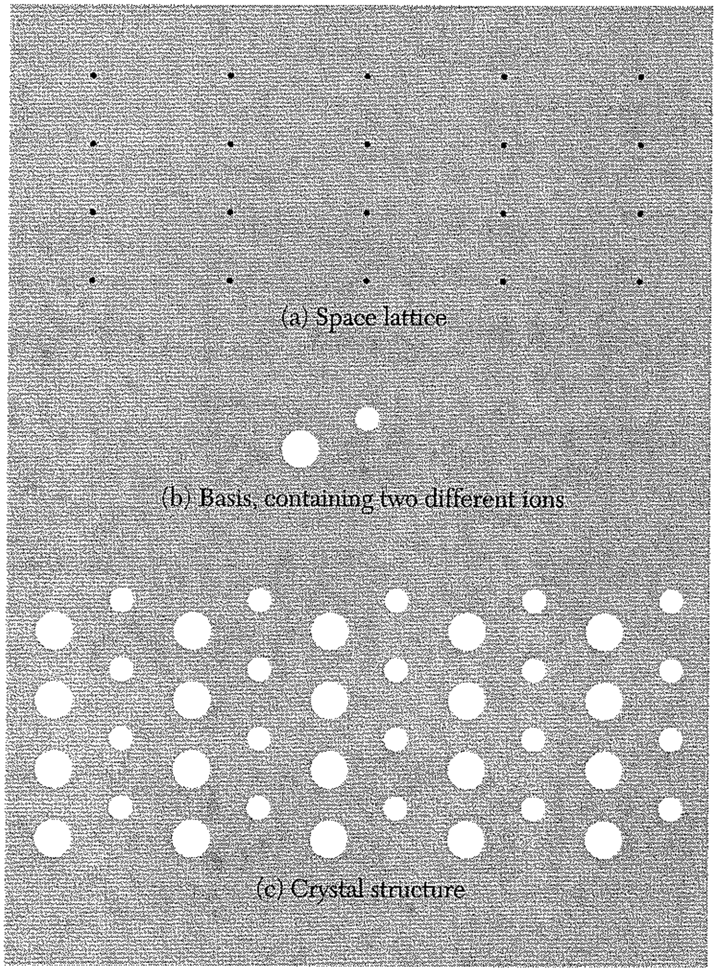


Figure 2 The crystal structure is formed by the addition of the basis (b) to every lattice point of the space lattice (a). By looking at (c), one can recognize the basis and then one can abstract the space lattice. It does not matter where the basis is put in relation to a lattice point.

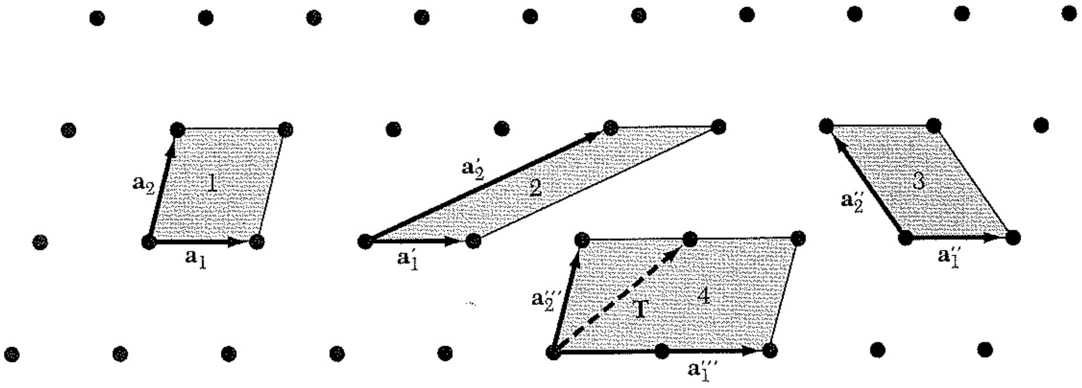
Basis and the Crystal Structure

The **basis** of the crystal structure can be identified once the crystal axes have been chosen. Figure 2 shows how a crystal is made by adding a basis to every lattice point—of course the lattice points are just mathematical constructions. Every basis in a given crystal is identical to every other in composition, arrangement, and orientation.

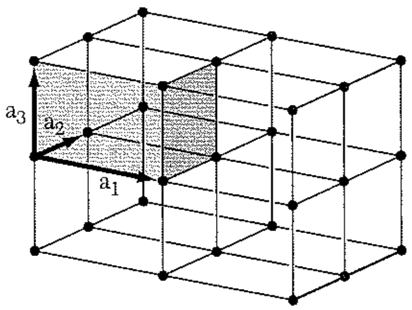
The number of atoms in the basis may be one, or it may be more than one. The position of the center of an atom j of the basis relative to the associated lattice point is

$$\mathbf{r}_j = x_j\mathbf{a}_1 + y_j\mathbf{a}_2 + z_j\mathbf{a}_3 \, . \tag{2}$$

We may arrange the origin, which we have called the associated lattice point, so that $0 \leq x_j, y_j, z_j \leq 1$.



(a)



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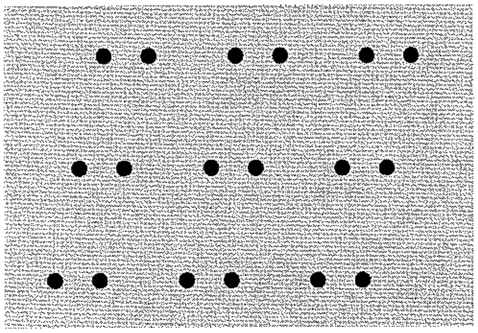


(c)

Figure 3a Lattice points of a space lattice in two dimensions. All pairs of vectors $\mathbf{a}_1$, $\mathbf{a}_2$ are translation vectors of the lattice. But $\mathbf{a}_1'''$, $\mathbf{a}_2'''$ are not primitive translation vectors because we cannot form the lattice translation **T** from integral combinations of $\mathbf{a}_1'''$ and $\mathbf{a}_2'''$. The other pairs shown of $\mathbf{a}_1$ and $\mathbf{a}_2$ may be taken as the primitive translation vectors of the lattice. The parallelograms 1, 2, 3 are equal in area and any of them could be taken as the primitive cell. The parallelogram 4 has twice the area of a primitive cell.

Figure 3b Primitive cell of a space lattice in three dimensions.

Figure 3c Suppose these points are identical atoms: Sketch in on the figure a set of lattice points, a choice of primitive axes, a primitive cell, and the basis of atoms associated with a lattice point.

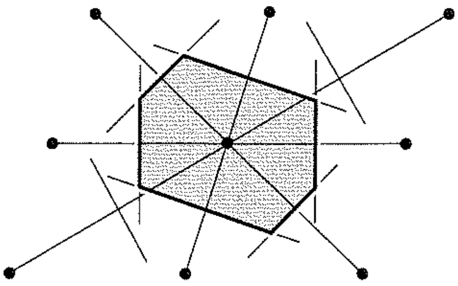


Figure 4 A primitive cell may also be chosen following this procedure: (1) draw lines to connect a given lattice point to all nearby lattice points; (2) at the midpoint and normal to these lines, draw new lines or planes. The smallest volume enclosed in this way is the Wigner-Seitz primitive cell. All space may be filled by these cells, just as by the cells of Fig. 3.

Primitive Lattice Cell

The parallelepiped defined by primitive axes $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ is called a **primitive cell** (Fig. 3b). A primitive cell is a type of cell or unit cell. (The adjective unit is superfluous and not needed.) A cell will fill all space by the repetition of suitable crystal translation operations. A primitive cell is a minimum-volume cell. There are many ways of choosing the primitive axes and primitive cell for a given lattice. The number of atoms in a primitive cell or primitive basis is always the same for a given crystal structure.

There is always one lattice point per primitive cell. If the primitive cell is a parallelepiped with lattice points at each of the eight corners, each lattice point is shared among eight cells, so that the total number of lattice points in the cell is one: $8 \times \frac{1}{8} = 1$. The volume of a parallelepiped with axes $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ is

$$V_c = |\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3| \ , \tag{3}$$

by elementary vector analysis. The basis associated with a primitive cell is called a primitive basis. No basis contains fewer atoms than a primitive basis contains. Another way of choosing a primitive cell is shown in Fig. 4. This is known to physicists as a **Wigner-Seitz cell.**

FUNDAMENTAL TYPES OF LATTICES

Crystal lattices can be carried or mapped into themselves by the lattice translations **T** and by various other symmetry operations. A typical symmetry operation is that of rotation about an axis that passes through a lattice point. Lattices can be found such that one-, two-, three-, four-, and sixfold rotation axes carry the lattice into itself, corresponding to rotations by 2π, $2\pi/2$, $2\pi/3$, $2\pi/4$, and $2\pi/6$ radians and by integral multiples of these rotations. The rotation axes are denoted by the symbols 1, 2, 3, 4, and 6.

We cannot find a lattice that goes into itself under other rotations, such as by $2\pi/7$ radians or $2\pi/5$ radians. A single molecule properly designed can have any degree of rotational symmetry, but an infinite periodic lattice cannot. We can make a crystal from molecules that individually have a fivefold rotation axis, but we should not expect the lattice to have a fivefold rotation axis. In Fig. 5 we show what happens if we try to construct a periodic lattice having fivefold

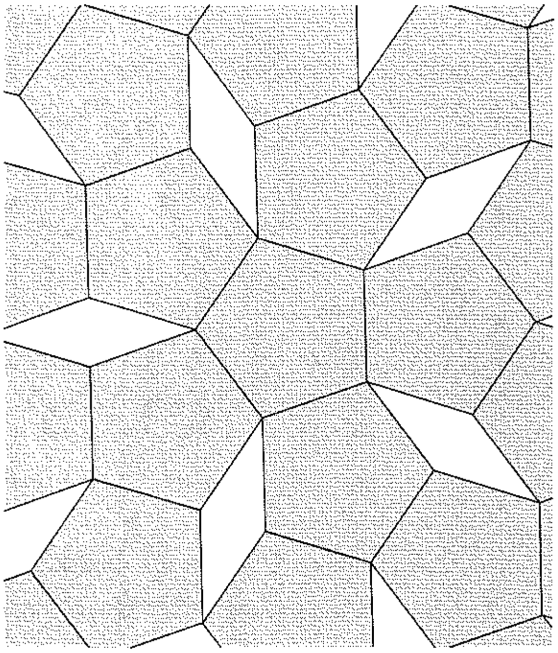


Figure 5 A fivefold axis of symmetry cannot exist in a periodic lattice because it is not possible to fill the area of a plane with a connected array of pentagons. We can, however, fill all the area of a plane with just two distinct designs of "tiles" or elementary polygons.

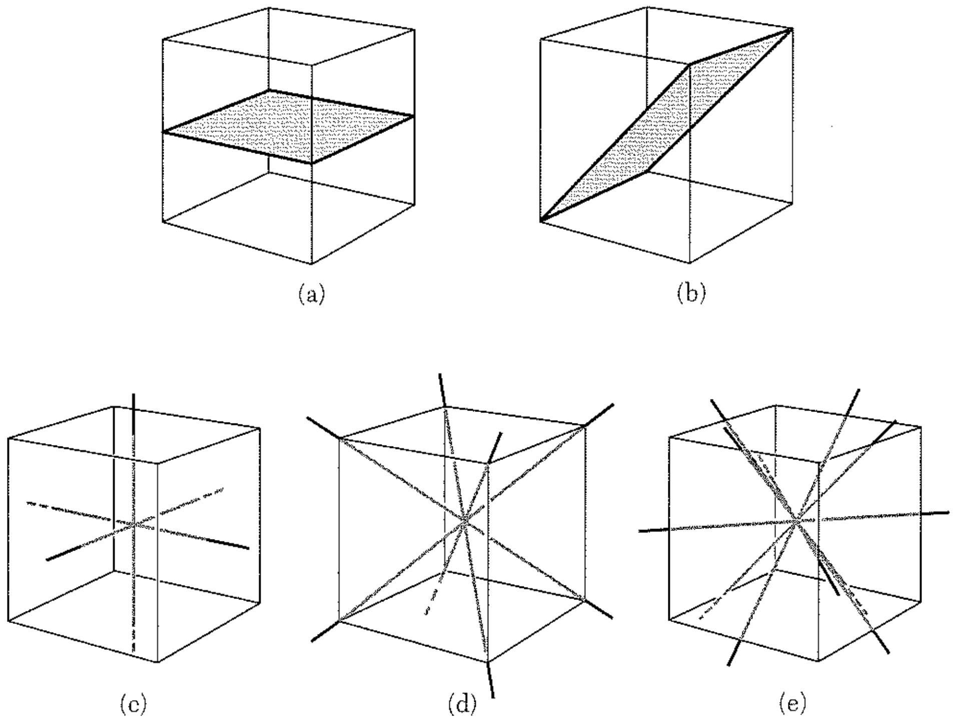


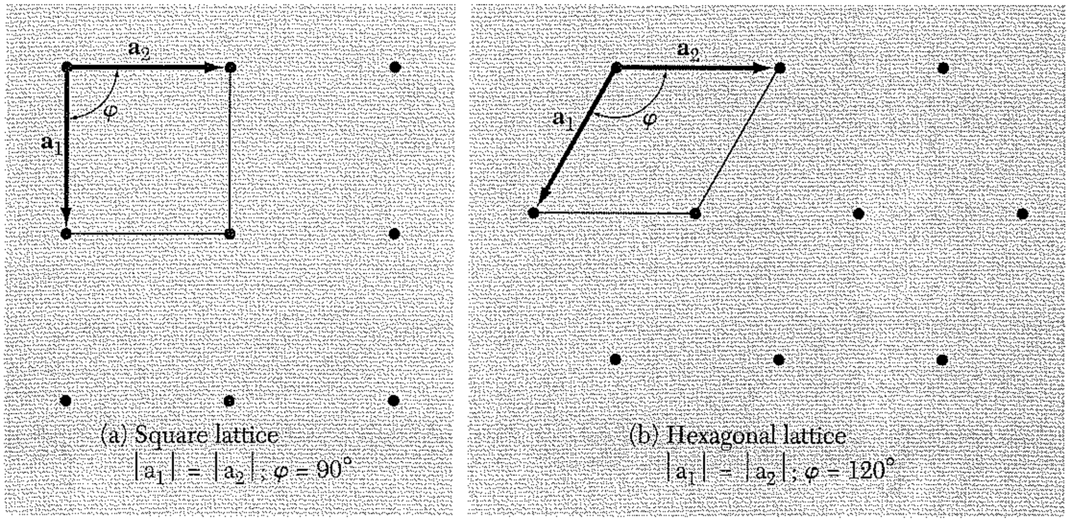
Figure 6 (a) A plane of symmetry parallel to the faces of a cube. (b) A diagonal plane of symmetry in a cube. (c) The three tetrad axes of a cube. (d) The four triad axes of a cube. (e) The six diad axes of a cube.

symmetry: the pentagons do not fit together to fill all space, showing that we cannot combine fivefold point symmetry with the required translational periodicity.

By lattice point group we mean the collection of symmetry operations which, applied about a lattice point, carry the lattice into itself. The possible rotations have been listed. We can have mirror reflections *m* about a plane through a lattice point. The inversion operation is composed of a rotation of π followed by reflection in a plane normal to the rotation axis; the total effect is to replace $\mathbf{r}$ by $-\mathbf{r}$. The symmetry axes and symmetry planes of a cube are shown in Fig. 6.

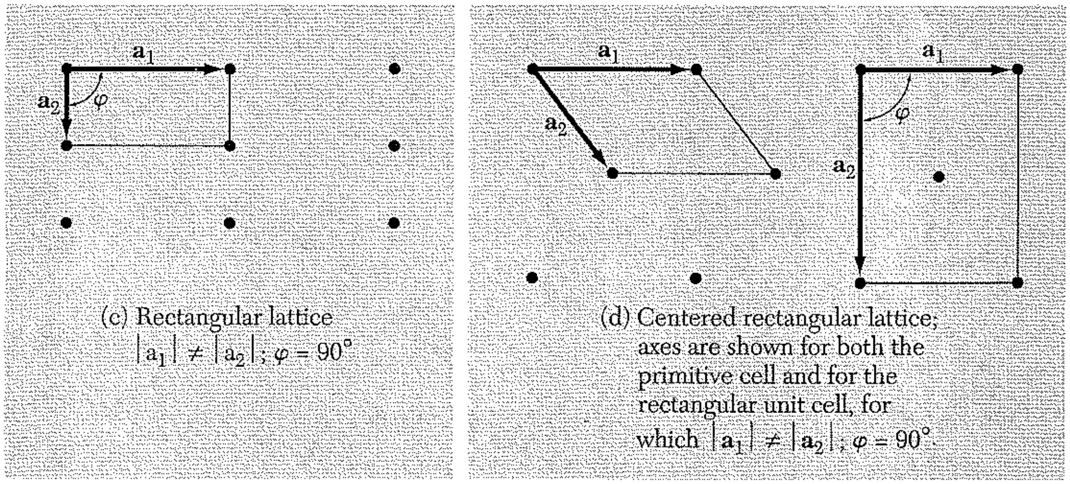
Two-Dimensional Lattice Types

The lattice in Fig. 3a was drawn for arbitrary $\mathbf{a}_1$ and $\mathbf{a}_2$. A general lattice such as this is known as an **oblique lattice** and is invariant only under rotation of π and 2π about any lattice point. But special lattices of the oblique type can be invariant under rotation of $2\pi/3$, $2\pi/4$, or $2\pi/6$, or under mirror reflection. We must impose restrictive conditions on $\mathbf{a}_1$ and $\mathbf{a}_2$ if we want to construct a lattice that will be invariant under one or more of these new operations. There are four distinct types of restriction, and each leads to what we may call a **special lattice type**. Thus there are five distinct lattice types in two dimensions, the oblique lattice and the four special lattices shown in Fig. 7. **Bravais lattice** is the common phrase for a distinct lattice type; we say that there are five Bravais lattices in two dimensions.



(a) Square lattice
$|\mathbf{a}_1| = |\mathbf{a}_2|$; $\varphi = 90°$

(b) Hexagonal lattice
$|\mathbf{a}_1| = |\mathbf{a}_2|$; $\varphi = 120°$



(c) Rectangular lattice
$|\mathbf{a}_1| \neq |\mathbf{a}_2|$; $\varphi = 90°$

(d) Centered rectangular lattice; axes are shown for both the primitive cell and for the rectangular unit cell, for which $|\mathbf{a}_1| \neq |\mathbf{a}_2|$; $\varphi = 90°$.

Figure 7 Four special lattices in two dimensions.

Three-Dimensional Lattice Types

The point symmetry groups in three dimensions require the 14 different lattice types listed in Table 1. The general lattice is triclinic, and there are 13 special lattices. These are grouped for convenience into systems classified according to seven types of cells, which are triclinic, monoclinic, orthorhombic, tetragonal, cubic, trigonal, and hexagonal. The division into systems is expressed in the table in terms of the axial relations that describe the cells. The cells in Fig. 8 are conventional cells: of these only the sc is a primitive cell. Often a nonprimitive cell has a more obvious relation with the point symmetry operations than has a primitive cell.

There are three lattices in the cubic system: the simple cubic (sc) lattice, the body-centered cubic (bcc) lattice, and the face-centered cubic (fcc) lattice.

Table 1 The 14 lattice types in three dimensions

System	Number of lattices	Restrictions on conventional cell axes and angles
Triclinic	1	$a_1 \neq a_2 \neq a_3$ $\alpha \neq \beta \neq \gamma$
Monoclinic	2	$a_1 \neq a_2 \neq a_3$ $\alpha = \gamma = 90^\circ \neq \beta$
Orthorhombic	4	$a_1 \neq a_2 \neq a_3$ $\alpha = \beta = \gamma = 90^\circ$
Tetragonal	2	$a_1 = a_2 \neq a_3$ $\alpha = \beta = \gamma = 90^\circ$
Cubic	3	$a_1 = a_2 = a_3$ $\alpha = \beta = \gamma = 90^\circ$
Trigonal	1	$a_1 = a_2 = a_3$ $\alpha = \beta = \gamma < 120^\circ, \neq 90^\circ$
Hexagonal	1	$a_1 = a_2 \neq a_3$ $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$

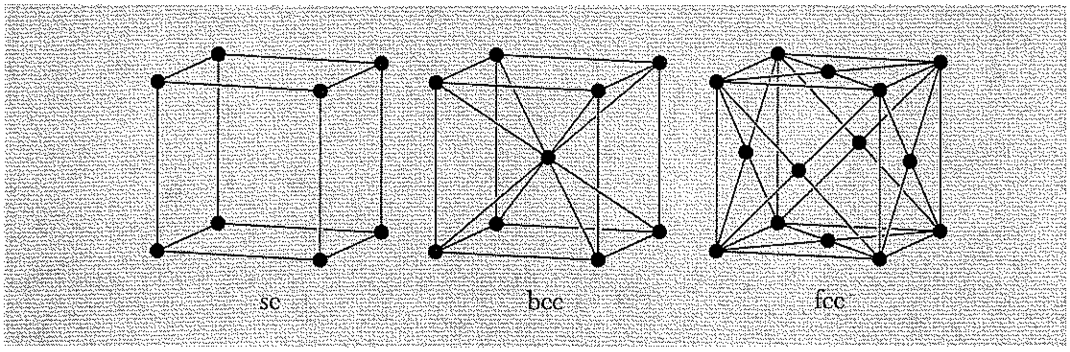


Figure 8 The cubic space lattices. The cells shown are the conventional cells.

Table 2 Characteristics of cubic lattices[a]

	Simple	Body-centered	Face-centered
Volume, conventional cell	a^3	a^3	a^3
Lattice points per cell	1	2	4
Volume, primitive cell	a^3	$\frac{1}{2}a^3$	$\frac{1}{4}a^3$
Lattice points per unit volume	$1/a^3$	$2/a^3$	$4/a^3$
Number of nearest neighbors	6	8	12
Nearest-neighbor distance	a	$3^{1/2}\,a/2 = 0.866a$	$a/2^{1/2} = 0.707a$
Number of second neighbors	12	6	6
Second neighbor distance	$2^{1/2}a$	a	a
Packing fraction[a]	$\frac{1}{6}\pi$ $=0.524$	$\frac{1}{8}\pi\sqrt{3}$ $=0.680$	$\frac{1}{6}\pi\sqrt{2}$ $=0.740$

[a] The packing fraction is the maximum proportion of the available volume that can be filled with hard spheres.

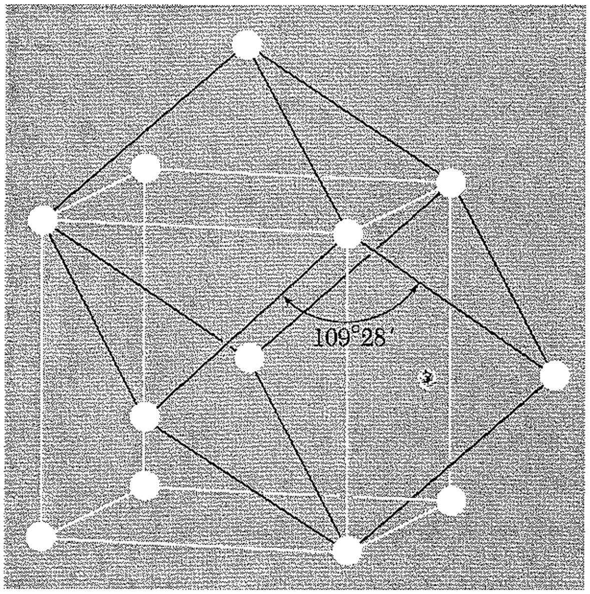


Figure 9 Body-centered cubic lattice, showing a primitive cell. The primitive cell shown is a rhombohedron of edge $\frac{1}{2}\sqrt{3}\,a$, and the angle between adjacent edges is 109°28′.

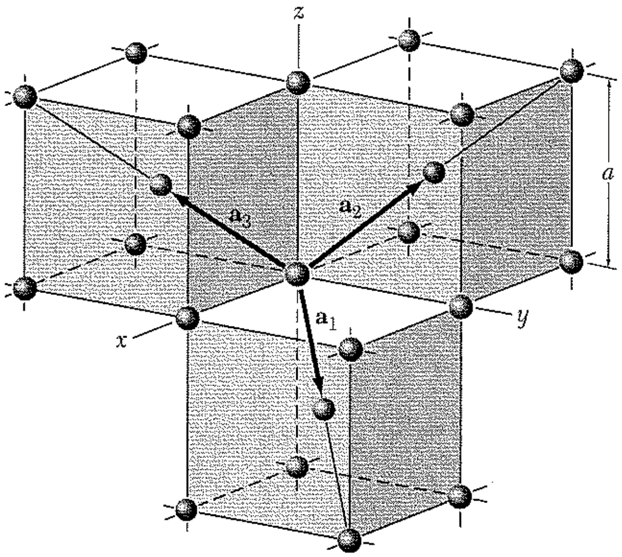


Figure 10 Primitive translation vectors of the body-centered cubic lattice; these vectors connect the lattice point at the origin to lattice points at the body centers. The primitive cell is obtained on completing the rhombohedron. In terms of the cube edge a, the primitive translation vectors are

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

Here $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, $\hat{\mathbf{z}}$ are the Cartesian unit vectors.

The characteristics of the three cubic lattices are summarized in Table 2. A primitive cell of the bcc lattice is shown in Fig. 9, and the primitive translation vectors are shown in Fig. 10. The primitive translation vectors of the fcc lattice are shown in Fig. 11. Primitive cells by definition contain only one lattice point, but the conventional bcc cell contains two lattice points, and the fcc cell contains four lattice points.

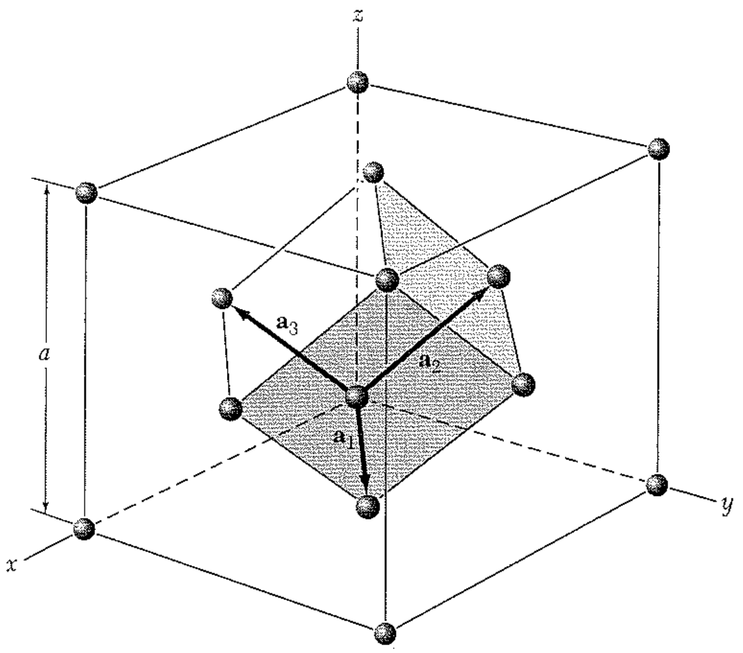


Figure 11 The rhombohedral primitive cell of the face-centered cubic crystal. The primitive translation vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ connect the lattice point at the origin with lattice points at the face centers. As drawn, the primitive vectors are:

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

The angles between the axes are 60°.

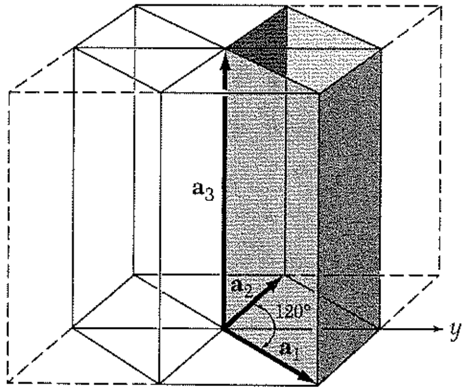


Figure 12 Relation of the primitive cell in the hexagonal system (heavy lines) to a prism of hexagonal symmetry. Here $a_1 = a_2 \neq a_3$.

The position of a point in a cell is specified by (2) in terms of the atomic coordinates x, y, z. Here each coordinate is a fraction of the axial length a_1, a_2, a_3 in the direction of the coordinate axis, with the origin taken at one corner of the cell. Thus the coordinates of the body center of a cell are $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, and the face centers include $\frac{1}{2}\frac{1}{2}0$, $0\frac{1}{2}\frac{1}{2}$; $\frac{1}{2}0\frac{1}{2}$. In the hexagonal system the primitive cell is a right prism based on a rhombus with an included angle of 120°. Figure 12 shows the relationship of the rhombic cell to a hexagonal prism.

INDEX SYSTEM FOR CRYSTAL PLANES

The orientation of a crystal plane is determined by three points in the plane, provided they are not collinear. If each point lay on a different crystal axis, the plane could be specified by giving the coordinates of the points in terms of the lattice constants a_1, a_2, a_3. However, it turns out to be more useful for structure analysis to specify the orientation of a plane by the indices determined by the following rules (Fig. 13).

- Find the intercepts on the axes in terms of the lattice constants a_1, a_2, a_3. The axes may be those of a primitive or nonprimitive cell.

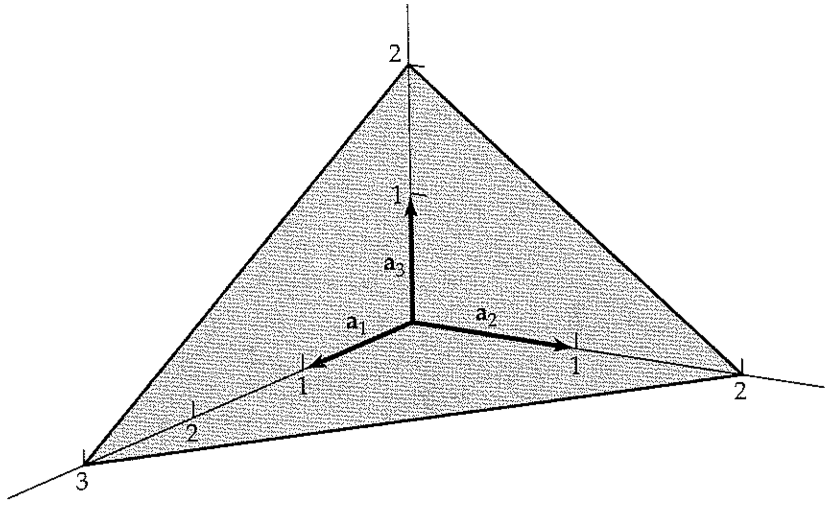
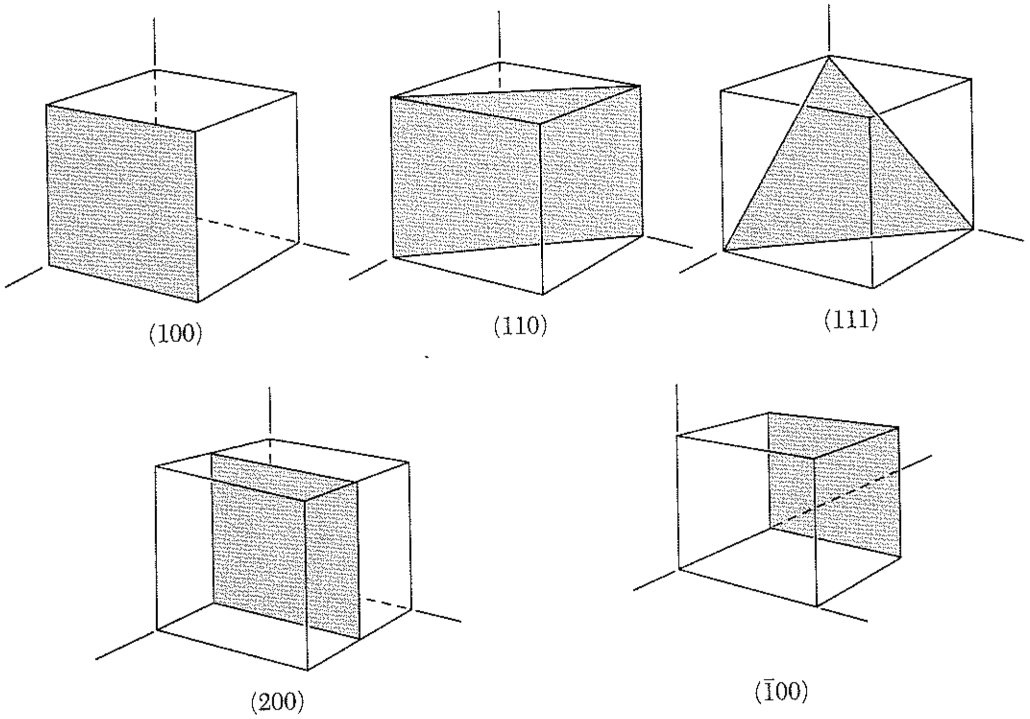


Figure 13 This plane intercepts the $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ axes at $3\mathbf{a}_1$, $2\mathbf{a}_2$, $2\mathbf{a}_3$. The reciprocals of these numbers are $\frac{1}{3}, \frac{1}{2}, \frac{1}{2}$. The smallest three integers having the same ratio are 2, 3, 3, and thus the indices of the plane are (233).


(100) (110) (111)

(200) ($\bar{1}00$)

Figure 14 Indices of important planes in a cubic crystal. The plane (200) is parallel to (100) and to (100).

- Take the reciprocals of these numbers and then reduce to three integers having the same ratio, usually the smallest three integers. The result, enclosed in parentheses (*hkl*), is called the index of the plane.

For the plane whose intercepts are 4, 1, 2, the reciprocals are $\frac{1}{4}$, 1, and $\frac{1}{2}$; the smallest three integers having the same ratio are (142). For an intercept at infinity, the corresponding index is zero. The indices of some important planes in a cubic crystal are illustrated by Fig. 14. The indices (*hkl*) may denote a single plane or a set of parallel planes. If a plane cuts an axis on the negative side of the origin, the corresponding index is negative, indicated by placing a minus sign above the index: $(hk\bar{l})$. The cube faces of a cubic crystal are (100), (010), (001), $(\bar{1}00)$, $(0\bar{1}0)$, and $(00\bar{1})$. Planes equivalent by symmetry may be denoted by curly brackets (braces) around indices; the set of cube faces is {100}. When we speak of the (200) plane we mean a plane parallel to (100) but cutting the $\mathbf{a}_1$ axis at $\frac{1}{2}a$.

The indices $[uvw]$ of a direction in a crystal are the set of the smallest integers that have the ratio of the components of a vector in the desired direction, referred to the axes. The $\mathbf{a}_1$ axis is the [100] direction; the $-\mathbf{a}_2$ axis is the $[0\bar{1}0]$ direction. In cubic crystals the direction $[hkl]$ is perpendicular to a plane (hkl) having the same indices, but this is not generally true in other crystal systems.

SIMPLE CRYSTAL STRUCTURES

We discuss simple crystal structures of general interest: the sodium chloride, cesium chloride, hexagonal close-packed, diamond, and cubic zinc sulfide structures.

Sodium Chloride Structure

The sodium chloride, NaCl, structure is shown in Figs. 15 and 16. The lattice is face-centered cubic; the basis consists of one Na^+ ion and one Cl^- ion

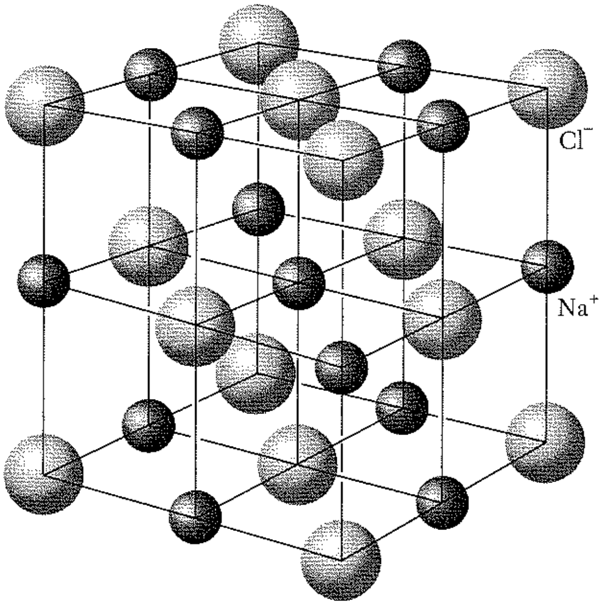


Figure 15 We may construct the sodium chloride crystal structure by arranging Na^+ and Cl^- ions alternately at the lattice points of a simple cubic lattice. In the crystal each ion is surrounded by six nearest neighbors of the opposite charge. The space lattice is fcc, and the basis has one Cl^- ion at 000 and one Na^+ ion at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. The figure shows one conventional cubic cell. The ionic diameters here are reduced in relation to the cell in order to clarify the spatial arrangement.

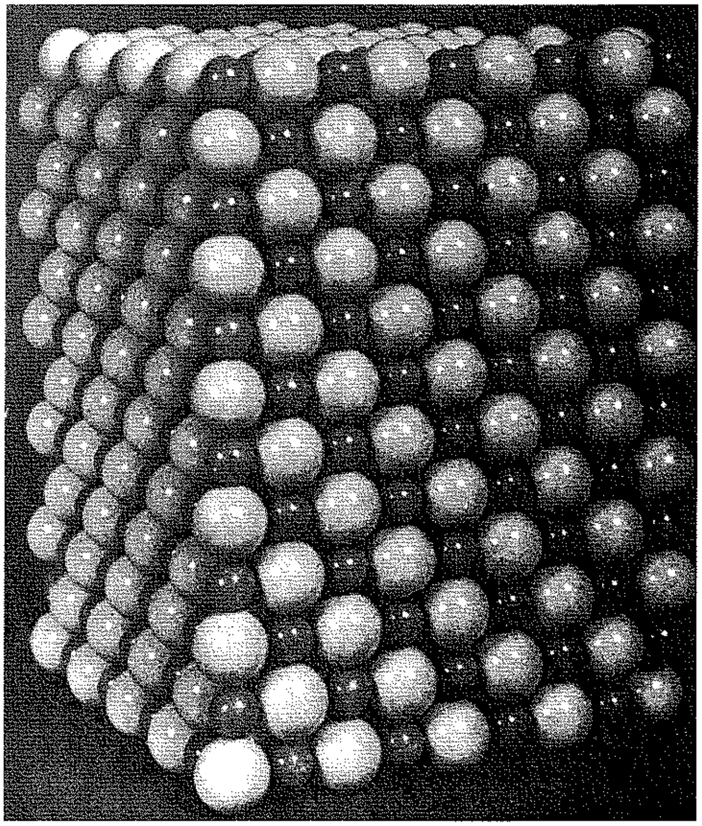


Figure 16 Model of sodium chloride. The sodium ions are smaller than the chlorine ions. (Courtesy of A. N. Holden and P. Singer.)

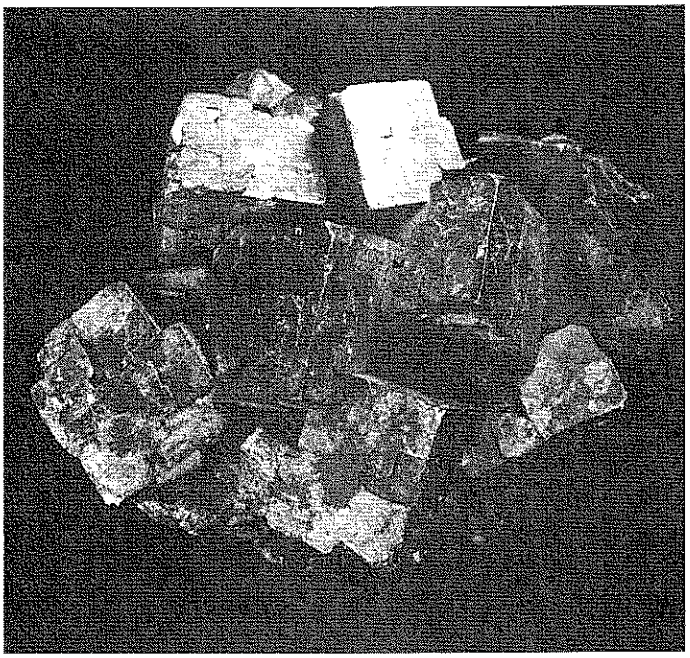


Figure 17 Natural crystals of lead sulfide, PbS, which has the NaCl crystal structure. (Photograph by B. Burleson.)

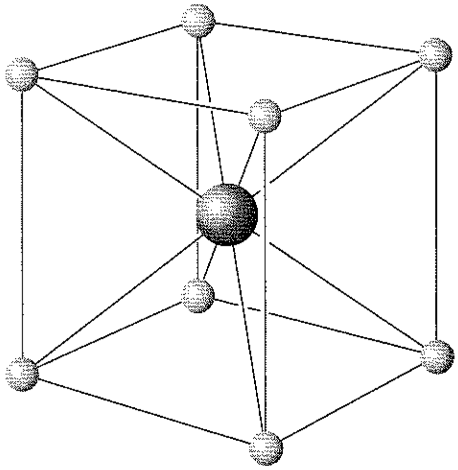


Figure 18 The cesium chloride crystal structure. The space lattice is simple cubic, and the basis has one Cs^+ ion at 000 and one Cl^- ion at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$.

separated by one-half the body diagonal of a unit cube. There are four units of NaCl in each unit cube, with atoms in the positions

Cl:	000 ;	$\frac{1}{2}\frac{1}{2}0$;	$\frac{1}{2}0\frac{1}{2}$;	$0\frac{1}{2}\frac{1}{2}$.
Na:	$\frac{1}{2}\frac{1}{2}\frac{1}{2}$;	$00\frac{1}{2}$;	$0\frac{1}{2}0$;	$\frac{1}{2}00$.

Each atom has as nearest neighbors six atoms of the opposite kind. Representative crystals having the NaCl arrangement include those in the following table. The cube edge a is given in angstroms; $1\ \text{Å} \equiv 10^{-8}$ cm $\equiv 10^{-10}$ m $\equiv 0.1$ nm. Figure 17 is a photograph of crystals of lead sulfide (PbS) from Joplin, Missouri. The Joplin specimens form in beautiful cubes.

Crystal	a	Crystal	a
LiH	4.08 Å	AgBr	5.77 Å
MgO	4.20	PbS	5.92
MnO	4.43	KCl	6.29
NaCl	5.63	KBr	6.59

Cesium Chloride Structure

The cesium chloride structure is shown in Fig. 18. There is one molecule per primitive cell, with atoms at the corners 000 and body-centered positions $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ of the simple cubic space lattice. Each atom may be viewed as at the center

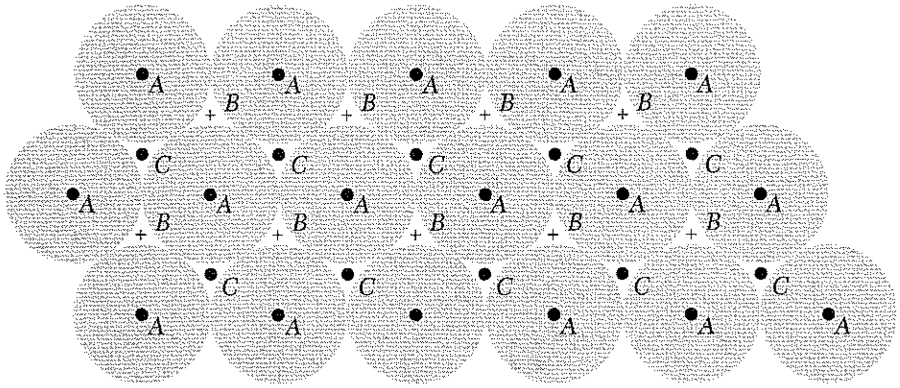


Figure 19 A close-packed layer of spheres is shown, with centers at points marked *A*. A second and identical layer of spheres can be placed on top of this, above and parallel to the plane of the drawing, with centers over the points marked *B*. There are two choices for a third layer. It can go in over *A* or over *C*. If it goes in over *A*, the sequence is *ABABAB* . . . and the structure is hexagonal close-packed. If the third layer goes in over *C*, the sequence is *ABCABCABC* . . . and the structure is face-centered cubic.

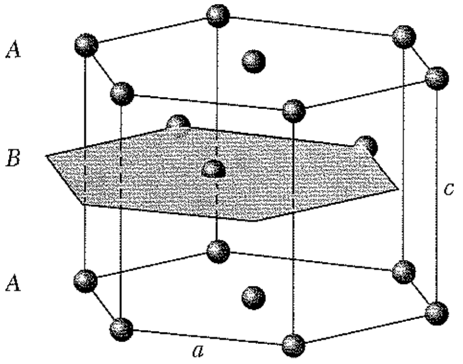


Figure 20 The hexagonal close-packed structure. The atom positions in this structure do not constitute a space lattice. The space lattice is simple hexagonal with a basis of two identical atoms associated with each lattice point. The lattice parameters a and c are indicated, where a is in the basal plane and c is the magnitude of the axis $\mathbf{a}_3$ of Fig. 12.

of a cube of atoms of the opposite kind, so that the number of nearest neighbors or coordination number is eight.

Crystal	a	Crystal	a
BeCu	2.70 Å	LiHg	3.29 Å
AlNi	2.88	NH_4Cl	3.87
CuZn (β-brass)	2.94	TlBr	3.97
CuPd	2.99	CsCl	4.11
AgMg	3.28	TlI	4.20

Hexagonal Close-Packed Structure (hcp)

There are an infinite number of ways of arranging identical spheres in a regular array that maximizes the packing fraction (Fig. 19). One is the face-centered cubic structure; another is the hexagonal close-packed structure (Fig. 20). The fraction of the total volume occupied by the spheres is 0.74 for both structures. No structure, regular or not, has denser packing.

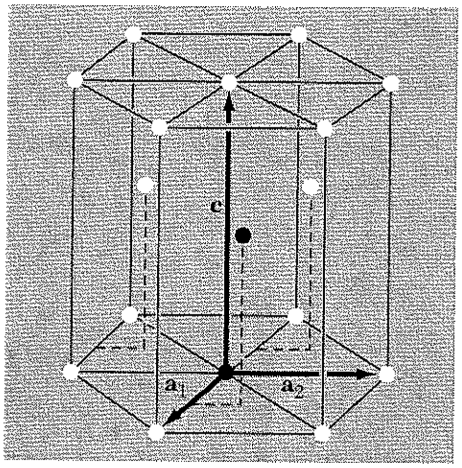


Figure 21 The primitive cell has $a_1 = a_2$, with an included angle of 120°. The c axis (or $\mathbf{a}_3$) is normal to the plane of $\mathbf{a}_1$ and $\mathbf{a}_2$. The ideal hcp structure has $c = 1.633\,a$. The two atoms of one basis are shown as solid circles. One atom of the basis is at the origin; the other atom is at $\frac{2}{3}\frac{1}{3}\frac{1}{2}$, which means at the position $\mathbf{r} = \frac{2}{3}\mathbf{a}_1 + \frac{1}{3}\mathbf{a}_2 + \frac{1}{2}\mathbf{a}_3$.

Spheres are arranged in a single closest-packed layer *A* by placing each sphere in contact with six others in a plane. This layer may serve as either the basal plane of an hcp structure or the (111) plane of the fcc structure. A second similar layer *B* may be added by placing each sphere of *B* in contact with three spheres of the bottom layer, as in Figs. 19–21. A third layer *C* may be added in two ways. We obtain the fcc structure if the spheres of the third layer are added over the holes in the first layer that are not occupied by *B*. We obtain the hcp structure when the spheres in the third layer are placed directly over the centers of the spheres in the first layer.

The number of nearest-neighbor atoms is 12 for both hcp and fcc structures. If the binding energy (or free energy) depended only on the number of nearest-neighbor bonds per atom, there would be no difference in energy between the fcc and hcp structures.

Crystal	c/a	Crystal	c/a	Crystal	c/a
He	1.633	Zn	1.861	Zr	1.594
Be	1.581	Cd	1.886	Gd	1.592
Mg	1.623	Co	1.622	Lu	1.586
Ti	1.586	Y	1.570		

Diamond Structure

The diamond structure is the structure of the semiconductors silicon and germanium and is related to the structure of several important semiconductor binary compounds. The space lattice of diamond is face-centered cubic. The primitive basis of the diamond structure has two identical atoms at coordinates 000 and $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ associated with each point of the fcc lattice, as shown in Fig. 22. Because the conventional unit cube of the fcc lattice contains 4 lattice points, it follows that the conventional unit cube of the diamond structure contains $2 \times 4 = 8$ atoms. There is no way to choose a primitive cell such that the basis of diamond contains only one atom.

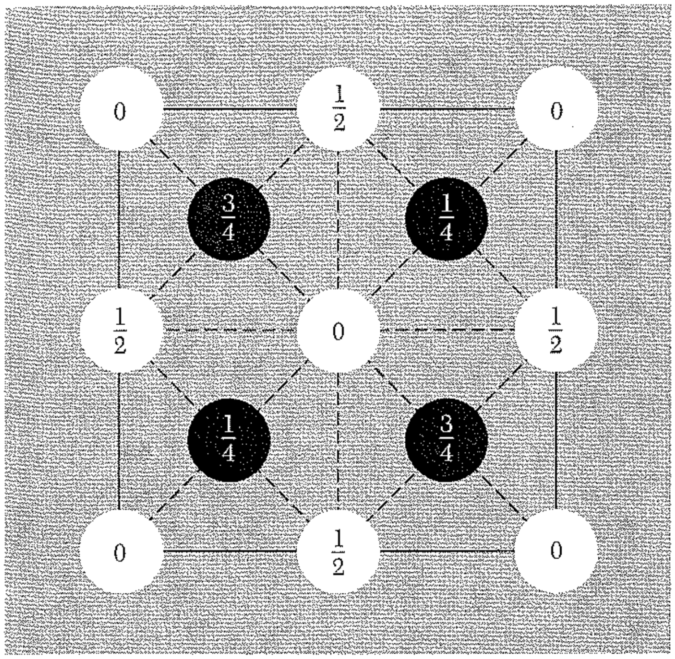


Figure 22 Atomic positions in the cubic cell of the diamond structure projected on a cube face; fractions denote height above the base in units of a cube edge. The points at 0 and $\frac{1}{2}$ are on the fcc lattice; those at $\frac{1}{4}$ and $\frac{3}{4}$ are on a similar lattice displaced along the body diagonal by one-fourth of its length. With a fcc space lattice, the basis consists of two identical atoms at 000 and $\frac{1}{4}\frac{1}{4}\frac{1}{4}$.

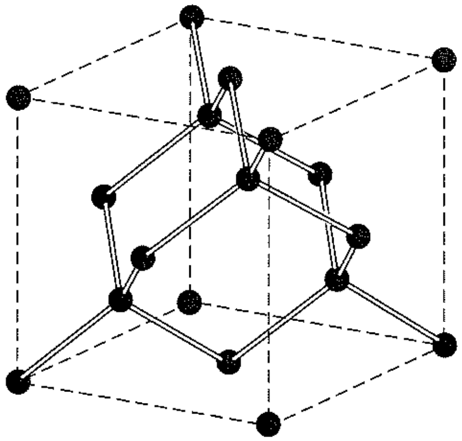


Figure 23 Crystal structure of diamond, showing the tetrahedral bond arrangement.

The tetrahedral bonding characteristic of the diamond structure is shown in Fig. 23. Each atom has 4 nearest neighbors and 12 next nearest neighbors. The diamond structure is relatively empty: the maximum proportion of the available volume which may be filled by hard spheres is only 0.34, which is 46 percent of the filling factor for a closest-packed structure such as fcc or hcp. The diamond structure is an example of the directional covalent bonding found in column IV of the periodic table of elements. Carbon, silicon, germanium, and tin can crystallize in the diamond structure, with lattice constants $a = 3.567$, 5.430, 5.658, and 6.49 Å, respectively. Here a is the edge of the conventional cubic cell.

Cubic Zinc Sulfide Structure

The diamond structure may be viewed as two fcc structures displaced from each other by one-quarter of a body diagonal. The cubic zinc sulfide (zinc blende) structure results when Zn atoms are placed on one fcc lattice and S atoms on the other fcc lattice, as in Fig. 24. The conventional cell is a cube. The coordinates of the Zn atoms are 000; $0\frac{1}{2}\frac{1}{2}$; $\frac{1}{2}0\frac{1}{2}$; $\frac{1}{2}\frac{1}{2}0$; the coordinates of the S atoms are $\frac{1}{4}\frac{1}{4}\frac{1}{4}$; $\frac{1}{4}\frac{3}{4}\frac{3}{4}$; $\frac{3}{4}\frac{1}{4}\frac{3}{4}$; $\frac{3}{4}\frac{3}{4}\frac{1}{4}$. The lattice is fcc. There are four molecules of ZnS per conventional cell. About each atom there are four equally distant atoms of the opposite kind arranged at the corners of a regular tetrahedron.

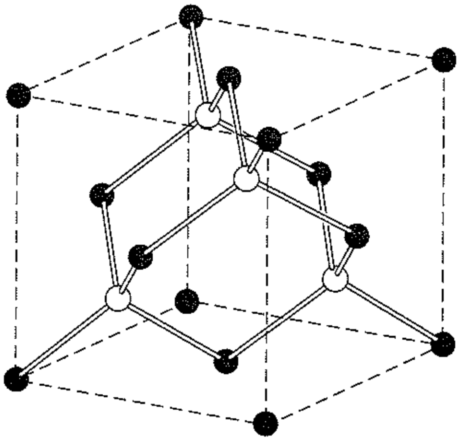


Figure 24 Crystal structure of cubic zinc sulfide.

The diamond structure allows a center-of-inversion symmetry operation at the midpoint of every line between nearest-neighbor atoms. The inversion operation carries an atom at $\mathbf{r}$ into an atom at $-\mathbf{r}$. The cubic ZnS structure does not have inversion symmetry. Examples of the cubic zinc sulfide structure are

Crystal	a	Crystal	a
SiC	4.35 Å	ZnSe	5.65 Å
ZnS	5.41	GaAs	5.65
AlP	5.45	AlAs	5.66
GaP	5.45	InSb	6.46

The close equality of the lattice constants of several pairs, notably (Al, Ga)P and (Al, Ga)As, makes possible the construction of semiconductor heterojunctions (Chapter 19).

DIRECT IMAGING OF ATOMIC STRUCTURE

Direct images of crystal structure have been produced by transmission electron microscopy. Perhaps the most beautiful images are produced by scanning tunneling microscopy; in STM (Chapter 19) one exploits the large variations in quantum tunneling as a function of the height of a fine metal tip above the surface of a crystal. The image of Fig. 25 was produced in this way. An STM method has been developed that will assemble single atoms into an organized layer nanometer structure on a crystal substrate.

NONIDEAL CRYSTAL STRUCTURES

The ideal crystal of classical crystallographers is formed by the periodic repetition of identical units in space. But no general proof has been given that

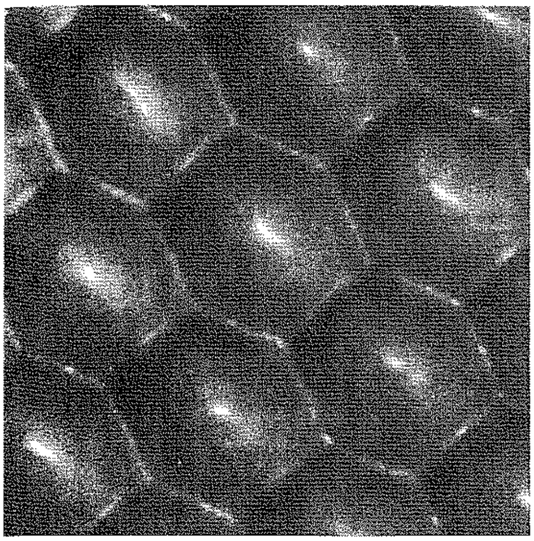


Figure 25 A scanning tunneling microscope image of atoms on a (111) surface of fcc platinum at 4 K. The nearest-neighbor spacing is 2.78 Å. (Photo courtesy of D. M. Eigler, IBM Research Division.)

the ideal crystal is the state of minimum energy of identical atoms at the temperature of absolute zero. At finite temperatures this is likely not to be true. We give a further example here.

Random Stacking and Polytypism

The fcc and hcp structures are made up of close-packed planes of atoms. The structures differ in the stacking sequence of the planes, fcc having the sequence *ABCABC* . . . and hcp having the sequence *ABABAB* . . . . Structures are known in which the stacking sequence of close-packed planes is random. This is known as **random stacking** and may be thought of as crystalline in two dimensions and noncrystalline or glasslike in the third.

Polytypism is characterized by a stacking sequence with a long repeat unit along the stacking axis. The best known example is zinc sulfide, ZnS, in which more than 150 polytypes have been identified, with the longest periodicity being 360 layers. Another example is silicon carbide, SiC, which occurs with more than 45 stacking sequences of the close-packed layers. The polytype of SiC known as 393R has a primitive cell with $a = 3.079$ Å and $c = 989.6$ Å. The longest primitive cell observed for SiC has a repeat distance of 594 layers. A given sequence is repeated many times within a single crystal. The mechanism that induces such long-range crystallographic order is not a long-range force, but arises from spiral steps due to dislocations in the growth nucleus (Chapter 20).

CRYSTAL STRUCTURE DATA

In Table 3 we list the more common crystal structures and lattice structures of the elements. Values of the atomic concentration and the density are given in Table 4. Many elements occur in several crystal structures and transform from

Table 3 Crystal structures of the elements

The data given are at room temperature for the most common form, or at the stated temperature in deg K. (Inorganic Crystal Structure Database (ICSD) online.

← Crystal structure →
← *a* lattice parameter, in Å →
← *c* lattice parameter, in Å →

H^1 4K hcp 3.75 6.12																	**He^4** 2K hcp 3.57 5.83
Li 78K bcc 3.491	**Be** hcp 2.27 3.59											**B** rhomb.	**C** diamond 3.567	**N** 20K cubic 5.66 (N_2)	**O** complex (O_2)	**F**	**Ne** 4K fcc 4.46
Na 5K bcc 4.225	**Mg** hcp 3.21 5.21											**Al** fcc 4.05	**Si** diamond 5.430	**P** complex	**S** complex	**Cl** complex (Cl_2)	**Ar** 4K fcc 5.31
K 5K bcc 5.225	**Ca** fcc 5.58	**Sc** hcp 3.31 5.27	**Ti** hcp 2.95 4.68	**V** bcc 3.03	**Cr** bcc 2.88	**Mn** cubic complex	**Fe** bcc 2.87	**Co** hcp 2.51 4.07	**Ni** fcc 3.52	**Cu** fcc 3.61	**Zn** hcp 2.66 4.95	**Ga** complex	**Ge** diamond 5.658	**As** rhomb.	**Se** hex. chains	**Br** complex (Br_2)	**Kr** 4K fcc 5.64
Rb 5K bcc 5.585	**Sr** fcc 6.08	**Y** hcp 3.65 5.73	**Zr** hcp 3.23 5.15	**Nb** bcc 3.30	**Mo** bcc 3.15	**Tc** hcp 2.74 4.40	**Ru** hcp 2.71 4.28	**Rh** fcc 3.80	**Pd** fcc 3.89	**Ag** fcc 4.09	**Cd** hcp 2.98 5.62	**In** tetr. 3.25 4.95	**Sn (α)** diamond 6.49	**Sb** rhomb.	**Te** hex. chains	**I** complex (I_2)	**Xe** 4K fcc 6.13
Cs 5K bcc 6.045	**Ba** bcc 5.02	**La** hex. 3.77 *ABAC*	**Hf** hcp 3.19 5.05	**Ta** bcc 3.30	**W** bcc 3.16	**Re** hcp 2.76 4.46	**Os** hcp 2.74 4.32	**Ir** fcc 3.84	**Pt** fcc 3.92	**Au** fcc 4.08	**Hg** rhomb.	**Tl** hcp 3.46 5.52	**Pb** fcc 4.95	**Bi** rhomb.	**Po** sc 3.34	**At** —	**Rn** —
Fr —	**Ra** —	**Ac** fcc 5.31															

Ce fcc 5.16	**Pr** hex. 3.67 *ABAC*	**Nd** hex. 3.66	**Pm** —	**Sm** complex	**Eu** bcc 4.58	**Gd** hcp 3.63 5.78	**Tb** hcp 3.60 5.70	**Dy** hcp 3.59 5.65	**Ho** hcp 3.58 5.62	**Er** hcp 3.56 5.59	**Tm** hcp 3.54 5.56	**Yb** fcc 5.48	**Lu** hcp 3.50 5.55
Th fcc 5.08	**Pa** tetr. 3.92 3.24	**U** complex	**Np** complex	**Pu** complex	**Am** hex. 3.64 *ABAC*	**Cm** —	**Bk** —	**Cf** —	**Es** —	**Fm** —	**Md** —	**No** —	**Lr** —

Table 4 Density and atomic concentration

The data are given at atmospheric pressure and room temperature, or at the stated temperature in deg K. (Crystal modifications as for Table 3.)

← Density in g cm^{-3} (10^3kg m^{-3}) →
← Concentration in 10^{22} cm^{-3} (10^{28} m^{-3}) →
← Nearest-neighbor distance, in Å (10^{-10}m) →

H 4K 0.088																	**He** 2K 0.205 (at 37 atm)
Li 78K 0.542 4.700 3.023	**Be** 1.82 12.1 2.22											**B** 2.47 13.0	**C** 3.516 17.6 1.54	**N** 20K 1.03	**O**	**F** 1.44	**Ne** 4K 1.51 4.36 3.16
Na 5K 1.013 2.652 3.659	**Mg** 1.74 4.30 3.20											**Al** 2.70 6.02 2.86	**Si** 2.33 5.00 2.35	**P**	**S**	**Cl** 93K 2.03 2.02	**Ar** 4K 1.77 2.66 3.76
K 5K 0.910 1.402 4.525	**Ca** 1.53 2.30 3.95	**Sc** 2.99 4.27 3.25	**Ti** 4.51 5.66 2.89	**V** 6.09 7.22 2.62	**Cr** 7.19 8.33 2.50	**Mn** 7.47 8.18 2.24	**Fe** 7.87 8.50 2.48	**Co** 8.9 8.97 2.50	**Ni** 8.91 9.14 2.49	**Cu** 8.93 8.45 2.56	**Zn** 7.13 6.55 2.66	**Ga** 5.91 5.10 2.44	**Ge** 5.32 4.42 2.45	**As** 5.77 4.65 3.16	**Se** 4.81 3.67 2.32	**Br** 123K 4.05 2.36	**Kr** 4K 3.09 2.17 4.00
Rb 5K 1.629 1.148 4.837	**Sr** 2.58 1.78 4.30	**Y** 4.48 3.02 3.55	**Zr** 6.51 4.29 3.17	**Nb** 8.58 5.56 2.86	**Mo** 10.22 6.42 2.72	**Tc** 11.50 7.04 2.71	**Ru** 12.36 7.36 2.65	**Rh** 12.42 7.26 2.69	**Pd** 12.00 6.80 2.75	**Ag** 10.50 5.85 2.89	**Cd** 8.65 4.64 2.98	**In** 7.29 3.83 3.25	**Sn** 5.76 2.91 2.81	**Sb** 6.69 3.31 2.91	**Te** 6.25 2.94 2.86	**I** 4.95 2.36 3.54	**Xe** 4K 3.78 1.64 4.34
Cs 5K 1.997 0.905 5.235	**Ba** 3.59 1.60 4.35	**La** 6.17 2.70 3.73	**Hf** 13.20 4.52 3.13	**Ta** 16.66 5.55 2.86	**W** 19.25 6.30 2.74	**Re** 21.03 6.80 2.74	**Os** 22.58 7.14 2.68	**Ir** 22.55 7.06 2.71	**Pt** 21.47 6.62 2.77	**Au** 19.28 5.90 2.88	**Hg** 227 14.26 4.26 3.01	**Tl** 11.87 3.50 3.46	**Pb** 11.34 3.30 3.50	**Bi** 9.80 2.82 3.07	**Po** 9.31 2.67 3.34	**At** —	**Rn** —
Fr —	**Ra** —	**Ac** 10.07 2.66 3.76															

Ce 6.77 2.91 3.65	**Pr** 6.78 2.92 3.63	**Nd** 7.00 2.93 3.66	**Pm** —	**Sm** 7.54 3.03 3.59	**Eu** 5.25 2.04 3.96	**Gd** 7.89 3.02 3.58	**Tb** 8.27 3.22 3.52	**Dy** 8.53 3.17 3.51	**Ho** 8.80 3.22 3.49	**Er** 9.04 3.26 3.47	**Tm** 9.32 3.32 3.54	**Yb** 6.97 3.02 3.88	**Lu** 9.84 3.39 3.43
Th 11.72 3.04 3.60	**Pa** 15.37 4.01 3.21	**U** 19.05 4.80 2.75	**Np** 20.45 5.20 2.62	**Pu** 19.81 4.26 3.1	**Am** 11.87 2.96 3.61	**Cm** —	**Bk** —	**Cf** —	**Es** —	**Fm** —	**Md** —	**No** —	**Lr** —

one to the other as the temperature or pressure is varied. Sometimes two structures coexist at the same temperature and pressure, although one may be slightly more stable.

SUMMARY

- A lattice is an array of points related by the lattice translation operator $\mathbf{T} = u_1\mathbf{a}_1 + u_2\mathbf{a}_2 + u_3\mathbf{a}_3$, where u_1, u_2, u_3 are integers and $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ are the crystal axes.
- To form a crystal we attach to every lattice point an identical basis composed of s atoms at the positions $\mathbf{r}_j = x_j\mathbf{a}_1 + y_j\mathbf{a}_2 + z_j\mathbf{a}_3$, with $j = 1, 2, \ldots, s$. Here x, y, z may be selected to have values between 0 and 1.
- The axes $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ are primitive for the minimum cell volume $|\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3|$ for which the crystal can be constructed from a lattice translation operator $\mathbf{T}$ and a basis at every lattice point.

Problems

1. ***Tetrahedral angles.*** The angles between the tetrahedral bonds of diamond are the same as the angles between the body diagonals of a cube, as in Fig. 10. Use elementary vector analysis to find the value of the angle. [illegible]
2. ***Indices of planes.*** Consider the planes with indices (100) and (001); the lattice is fcc, and the indices refer to the conventional cubic cell. What are the indices of these planes when referred to the primitive axes of Fig. 11?
3. ***Hcp structure.*** Show that the c/a ratio for an ideal hexagonal close-packed structure is $(\frac{8}{3})^{1/2} = 1.633$. If c/a is significantly larger than this value, the crystal structure may be thought of as composed of planes of closely packed atoms, the planes being loosely stacked.

2

Wave Diffraction and the Reciprocal Lattice

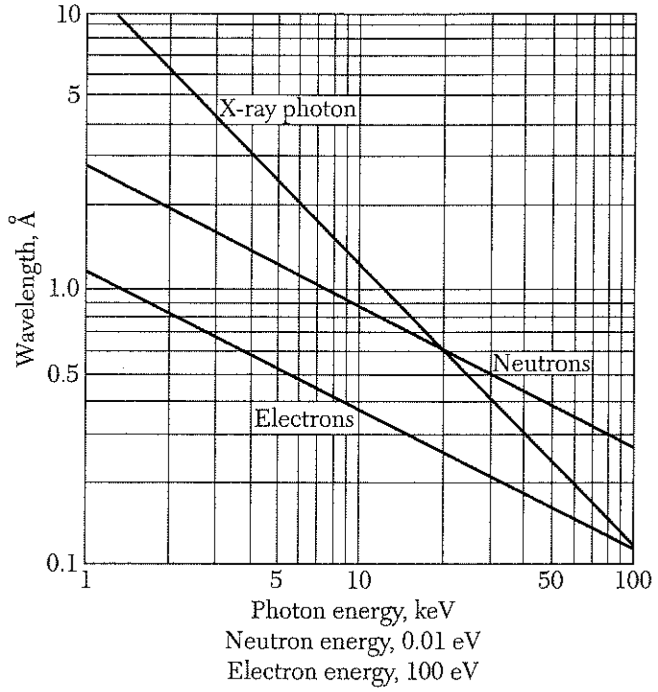


Figure 1 Wavelength versus particle energy, for photons, neutrons, and electrons.

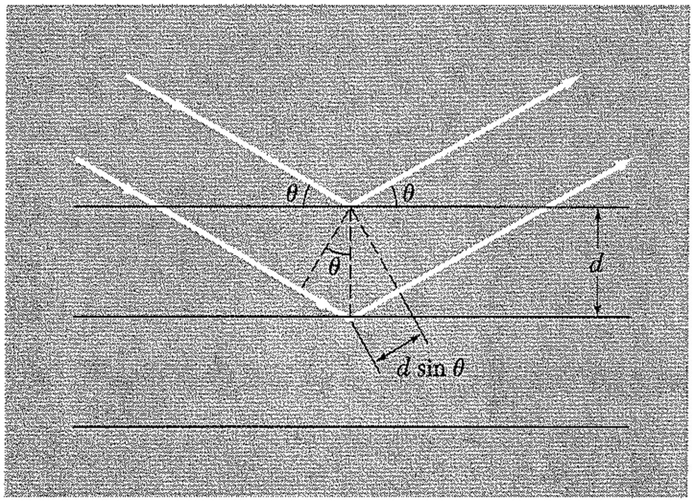


Figure 2 Derivation of the Bragg equation $2d \sin \theta = n\lambda$; here d is the spacing of parallel atomic planes and $2\pi n$ is the difference in phase between reflections from successive planes. The reflecting planes have nothing to do with the surface planes bounding the particular specimen.

CHAPTER 2: WAVE DIFFRACTION AND THE RECIPROCAL LATTICE

DIFFRACTION OF WAVES BY CRYSTALS

The Bragg law

We study crystal structure through the diffraction of photons, neutrons, and electrons (Fig. 1). The diffraction depends on the crystal structure and on the wavelength. At optical wavelengths such as 5000 Å, the superposition of the waves scattered elastically by the individual atoms of a crystal results in ordinary optical refraction. When the wavelength of the radiation is comparable with or smaller than the lattice constant, we may find diffracted beams in directions quite different from the incident direction.

W. L. Bragg presented a simple explanation of the diffracted beams from a crystal. The Bragg derivation is simple but is convincing only because it reproduces the correct result. Suppose that the incident waves are reflected specularly from parallel planes of atoms in the crystal, with each plane reflecting only a very small fraction of the radiation, like a lightly silvered mirror. In specular (mirrorlike) reflection the angle of incidence is equal to the angle of reflection. The diffracted beams are found when the reflections from parallel planes of atoms interfere constructively, as in Fig. 2. We treat elastic scattering, in which the energy of the x-ray is not changed on reflection.

Consider parallel lattice planes spaced d apart. The radiation is incident in the plane of the paper. The path difference for rays reflected from adjacent planes is $2d \sin \theta$, where θ is measured from the plane. Constructive interference of the radiation from successive planes occurs when the path difference is an integral number n of wavelengths λ, so that

$$2d \sin \theta = n\lambda \ . \qquad (1)$$

This is the Bragg law, which can be satisfied only for wavelength $\lambda \leq 2d$.

Although the reflection from each plane is specular, for only certain values of θ will the reflections from all periodic parallel planes add up in phase to give a strong reflected beam. If each plane were perfectly reflecting, only the first plane of a parallel set would see the radiation, and any wavelength would be reflected. But each plane reflects 10^{-3} to 10^{-5} of the incident radiation, so that 10^3 to 10^5 planes may contribute to the formation of the Bragg-reflected beam in a perfect crystal. Reflection by a single plane of atoms is treated in Chapter 17 on surface physics.

The Bragg law is a consequence of the periodicity of the lattice. Notice that the law does not refer to the composition of the basis of atoms associated

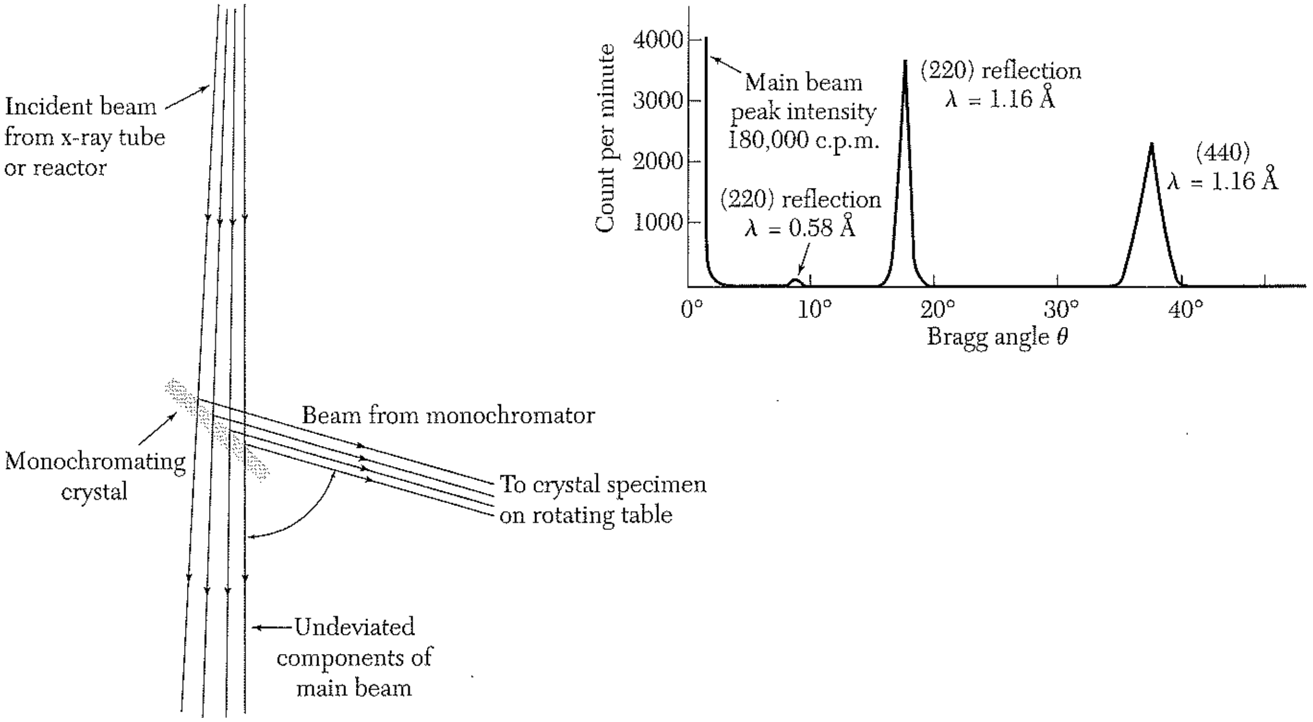


Figure 3 Sketch of a monochromator which by Bragg reflection selects a narrow spectrum of x-ray or neutron wavelengths from a broad spectrum incident beam. The upper part of the figure shows the analysis (obtained by reflection from a second crystal) of the purity of a 1.16 Å beam of neutrons from a calcium fluoride crystal monochromator. (After G. Bacon.)

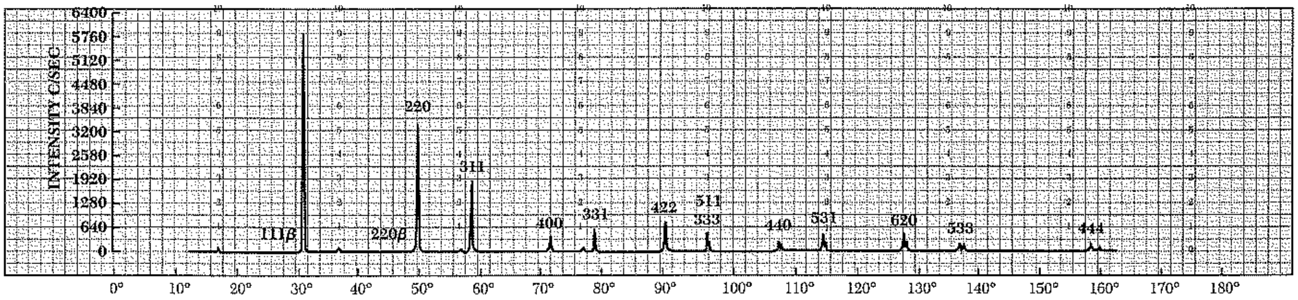


Figure 4 X-ray diffractometer recording of powdered silicon, showing a counter recording of the diffracted beams. (Courtesy of W. Parrish.)

with every lattice point. We shall see, however, that the composition of the basis determines the relative intensity of the various orders of diffraction (denoted by n above) from a given set of parallel planes. Bragg reflection from a single crystal is shown in Fig. 3 and from a powder in Fig. 4.

SCATTERED WAVE AMPLITUDE

The Bragg derivation of the diffraction condition (1) gives a neat statement of the condition for the constructive interference of waves scattered from the lattice points. We need a deeper analysis to determine the scattering intensity from the basis of atoms, which means from the spatial distribution of electrons within each cell.

Fourier Analysis

We have seen that a crystal is invariant under any translation of the form $\mathbf{T} = u_1\mathbf{a}_1 + u_2\mathbf{a}_2 + u_3\mathbf{a}_3$, where u_1, u_2, u_3 are integers and $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ are the crystal axes. Any local physical property of the crystal, such as the charge concentration, electron number density, or magnetic moment density is invariant under $\mathbf{T}$. What is most important to us here is that the electron number density $n(\mathbf{r})$ is a periodic function of $\mathbf{r}$, with periods $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ in the directions of the three crystal axes, respectively. Thus

$$n(\mathbf{r} + \mathbf{T}) = n(\mathbf{r}) \ . \tag{2}$$

Such periodicity creates an ideal situation for Fourier analysis. The most interesting properties of crystals are directly related to the Fourier components of the electron density.

We consider first a function $n(x)$ in one dimension with period a in the direction x. We expand $n(x)$ in a Fourier series of sines and cosines:

$$n(x) = n_0 + \sum_{p>0} \left[C_p \cos(2\pi px/a) + S_p \sin(2\pi px/a)\right] \ , \tag{3}$$

where the p are positive integers and C_p, S_p are real constants, called the Fourier coefficients of the expansion. The factor $2\pi/a$ in the arguments ensures that $n(x)$ has the period a:

$$\begin{aligned} n(x + a) &= n_0 + \sum[C_p \cos(2\pi px/a + 2\pi p) + S_p \sin(2\pi px/a + 2\pi p)] \\ &= n_0 + \sum[C_p \cos(2\pi px/a) + S_p \sin(2\pi px/a)] = n(x) \ . \end{aligned} \tag{4}$$

We say that $2\pi p/a$ is a point in the reciprocal lattice or Fourier space of the crystal. In one dimension these points lie on a line. The **reciprocal lattice points** tell us the allowed terms in the Fourier series (4) or (5). A term is allowed if it is consistent with the periodicity of the crystal, as in Fig. 5; other

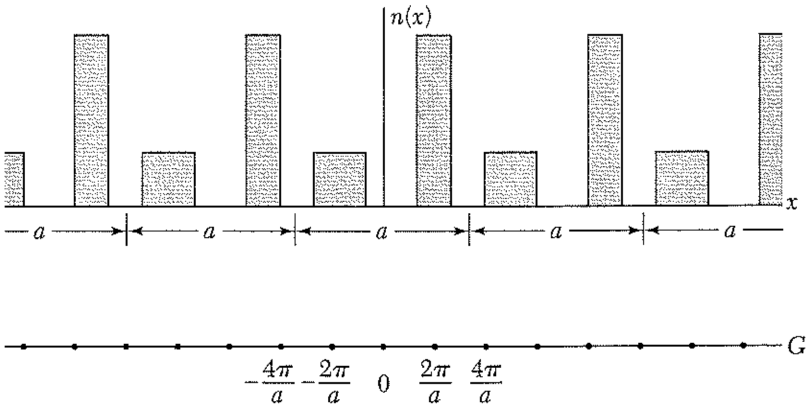


Figure 5 A periodic function $n(x)$ of period a, and the terms $2\pi p/a$ that may appear in the Fourier transform $n(x) = \sum n_p \exp(i2\pi px/a)$.

points in the reciprocal space are not allowed in the Fourier expansion of a periodic function.

It is convenient to write the series (4) in the compact form

$$n(x) = \sum_p n_p \exp(i2\pi px/a) \ , \tag{5}$$

where the sum is over all integers p: positive, negative, and zero. The coefficients n_p now are complex numbers. To ensure that $n(x)$ is a real function, we require

$$n^*_{-p} = n_p \ , \tag{6}$$

for then the sum of the terms in p and $-p$ is real. The asterisk on n^*_{-p} denotes the complex conjugate of n_{-p}.

With $\varphi = 2\pi px/a$, the sum of the terms in p and $-p$ in (5) is real if (6) is satisfied. The sum is

$$\begin{aligned} &n_p(\cos\varphi + i\sin\varphi) + n_{-p}(\cos\varphi - i\sin\varphi) \\ &\qquad = (n_p + n_{-p})\cos\varphi + i(n_p - n_{-p})\sin\varphi \ , \end{aligned} \tag{7}$$

which in turn is equal to the real function

$$2\mathrm{Re}\{n_p\}\cos\varphi - 2\mathrm{Im}\{n_p\}\sin\varphi \tag{8}$$

if (6) is satisfied. Here $\mathrm{Re}\{n_p\}$ and $\mathrm{Im}\{n_p\}$ are real and denote the real and imaginary parts of n_p. Thus the number density $n(x)$ is a real function, as desired.

The extension of the Fourier analysis to periodic functions $n(\mathbf{r})$ in three dimensions is straightforward. We must find a set of vectors $\mathbf{G}$ such that

$$n(\mathbf{r}) = \sum_{\mathbf{G}} n_{\mathbf{G}} \exp(i\mathbf{G}\cdot\mathbf{r}) \tag{9}$$

is invariant under all crystal translations $\mathbf{T}$ that leave the crystal invariant. It will be shown below that the set of Fourier coefficients $n_{\mathbf{G}}$ determines the x-ray scattering amplitude.

Inversion of Fourier Series. We now show that the Fourier coefficient n_p in the series (5) is given by

$$n_p = a^{-1}\int_0^a dx\, n(x)\exp(-i2\pi px/a) \ . \tag{10}$$

Substitute (5) in (10) to obtain

$$n_p = a^{-1}\sum_{p'} n_{p'} \int_0^a dx\, \exp[i2\pi(p'-p)x/a] \ . \tag{11}$$

If $p' \neq p$ the value of the integral is

$$\frac{a}{i2\pi(p'-p)}(e^{i2\pi(p'-p)}-1)=0 \ ,$$

because $p'-p$ is an integer and $\exp[i2\pi(\text{integer})] = 1$. For the term $p' = p$ the integrand is $\exp(i0) = 1$, and the value of the integral is a, so that $n_p = a^{-1}n_p a = n_p$, which is an identity, so that (10) is an identity.

As in (10), the inversion of (9) gives

$$n_{\mathbf{G}} = V_c^{-1}\int_{\text{cell}} dV\, n(\mathbf{r})\exp(-i\mathbf{G}\cdot\mathbf{r}) \ . \tag{12}$$

Here V_c is the volume of a cell of the crystal.

Reciprocal Lattice Vectors

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). There is a powerful, somewhat abstract procedure for doing this. The procedure forms the theoretical basis for much of solid state physics, where Fourier analysis is the order of the day.

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

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

The factors 2π are not used by crystallographers but are convenient in solid state physics.

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.

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, $n(\mathbf{r}+\mathbf{T}) = n(\mathbf{r}) = \sum n_\mathbf{G}\exp(i\mathbf{G}\cdot\mathbf{r})$.

Every crystal structure has two lattices associated with it, the crystal lattice and the reciprocal lattice. A diffraction pattern of a crystal is, as we shall show, a map of the reciprocal lattice of the crystal. A microscope image, if it could be resolved on a fine enough scale, is a map of the crystal structure in real space. The two lattices are related by the definitions (13). Thus when we rotate a crystal in a holder, we rotate both the direct lattice and the reciprocal lattice.

Vectors in the direct lattice have the dimensions of [length]; vectors in the reciprocal lattice have the dimensions of [1/length]. The reciprocal lattice is a lattice in the Fourier space associated with the crystal. The term is motivated below. Wavevectors are always drawn in Fourier space, so that every position in Fourier space may have a meaning as a description of a wave, but there is a special significance to the points defined by the set of **G**'s associated with a crystal structure.

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 wavevectors of the incoming and outgoing beams are **k** and **k**′. We suppose that the amplitude

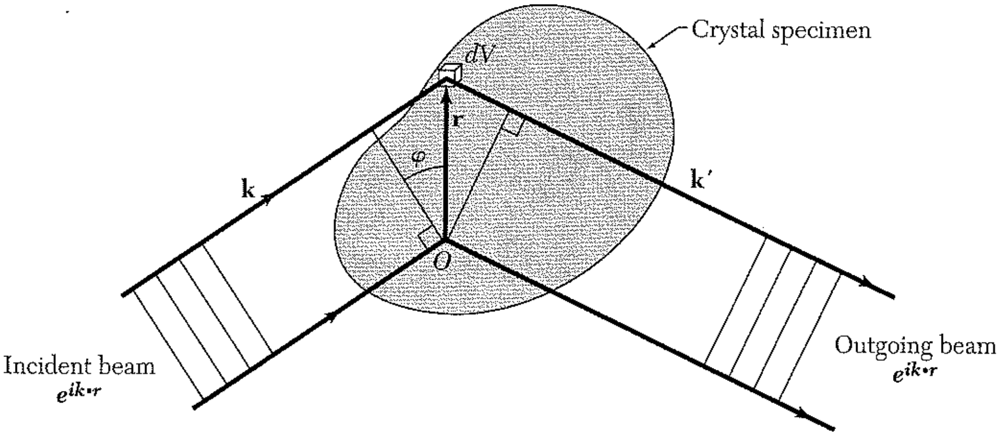


Figure 6 The difference in path length of the incident wave **k** at the points O, **r** is $r\sin\varphi$, and the difference in phase angle is $(2\pi r\sin\varphi)/\lambda$, which is equal to $\mathbf{k}\cdot\mathbf{r}$. For the diffracted wave the difference in phase angle is $-\mathbf{k}'\cdot\mathbf{r}$. 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.

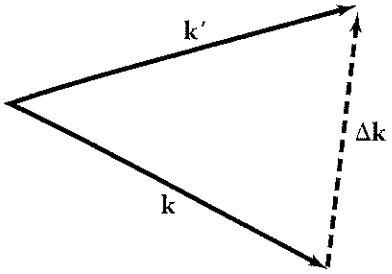


Figure 7 Definition of the scattering vector $\Delta\mathbf{k}$ such that $\mathbf{k} + \Delta\mathbf{k} = \mathbf{k}'$. In elastic scattering the magnitudes satisfy $k' = k$. Further, in Bragg scattering from a periodic lattice, any allowed $\Delta\mathbf{k}$ must equal some reciprocal lattice vector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

of the wave scattered from a volume element is proportional to the local electron concentration $n(\mathbf{r})$. 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 $\exp[i(\mathbf{k} - \mathbf{k}')\cdot\mathbf{r}]$.

In other words, the amplitude of the electric or magnetic field vectors in the scattered electromagnetic wave is proportional to the following integral which defines the quantity F that we call the **scattering amplitude**:

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

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

$$\mathbf{k} + \Delta\mathbf{k} = \mathbf{k}' \ . \tag{19}$$

Here $\Delta\mathbf{k}$ measures the change in wavevector and is called the **scattering vector** (Fig. 7). We add $\Delta\mathbf{k}$ to $\mathbf{k}$ to obtain $\mathbf{k}'$, the wavevector of the scattered beam.

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,

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

the argument of the exponential vanishes and $F = Vn_G$. It is a simple exercise (Problem 4) to show that F is negligibly small when $\Delta\mathbf{k}$ differs significantly from any reciprocal lattice vector.

In elastic scattering of a photon its energy $\hbar\omega$ is conserved, so that the frequency $\omega' = ck'$ of the emergent beam is equal to the frequency of the incident beam. 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. From (21) we found $\Delta\mathbf{k} = \mathbf{G}$ or $\mathbf{k} + \mathbf{G} = \mathbf{k}'$, so that the **diffraction condition** is written as $(\mathbf{k} + \mathbf{G})^2 = k^2$, or

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

This is the central result of the theory of elastic scattering of waves in a periodic lattice. If $\mathbf{G}$ is a reciprocal lattice vector, so is $-\mathbf{G}$, and with this substitution we can write (22) as

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

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

$$2(2\pi/\lambda) \sin\theta = 2\pi/d(hkl) \ ,$$

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. These are valuable because of their geometrical representation. 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.

A beautiful construction, the Ewald construction, is exhibited in Fig. 8. This helps us visualize the nature of the accident that must occur in order to satisfy the diffraction condition in three dimensions.

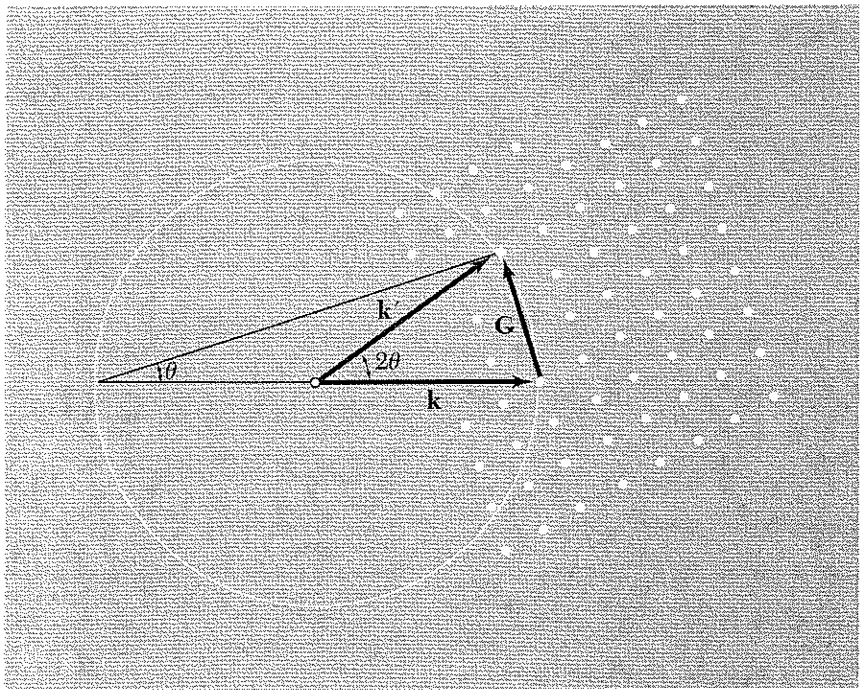


Figure 8 The points on the right-hand side are reciprocal-lattice points of the crystal. The vector **k** is drawn in the direction of the incident x-ray beam, and the origin is chosen such that **k** terminates at any reciprocal lattice point. We draw a sphere of radius $k = 2\pi/\lambda$ about the 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

Brillouin gave the statement of the diffraction condition that is most widely used in solid state physics, which means in the description of electron energy band theory and of the elementary excitations of other kinds. A Brillouin zone is defined as a Wigner-Seitz primitive cell in the reciprocal lattice. (The construction in the direct lattice was shown in Fig. 1.4.) The Brillouin zone gives a vivid geometrical interpretation of the diffraction condition $2\mathbf{k} \cdot \mathbf{G} = G^2$ of Eq. (23). We divide both sides by 4 to obtain

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

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.

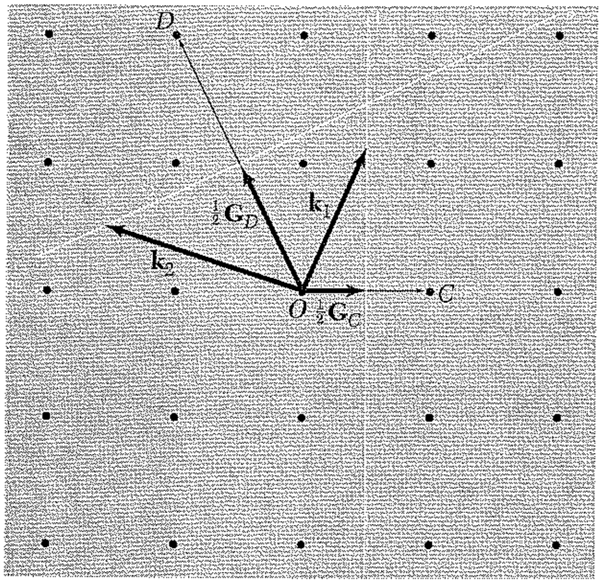


Figure 9a Reciprocal lattice points near the point O at the origin of the reciprocal lattice. The reciprocal lattice vector $\mathbf{G}_C$ connects points OC; and $\mathbf{G}_D$ connects OD. Two planes 1 and 2 are drawn which are the perpendicular bisectors of $\mathbf{G}_C$ and $\mathbf{G}_D$, respectively.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

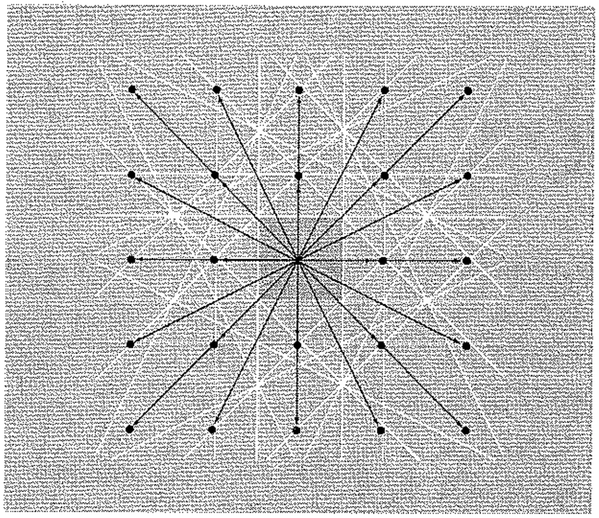


Figure 9b Square reciprocal lattice with reciprocal lattice vectors shown as fine black lines. The lines shown in white are perpendicular bisectors of the reciprocal lattice vectors. The central square is the smallest volume about the origin which is bounded entirely by white lines. The square is the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

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.

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.* Examples are shown in Figs. 10 and 11.

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.

Reciprocal Lattice to sc Lattice

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

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

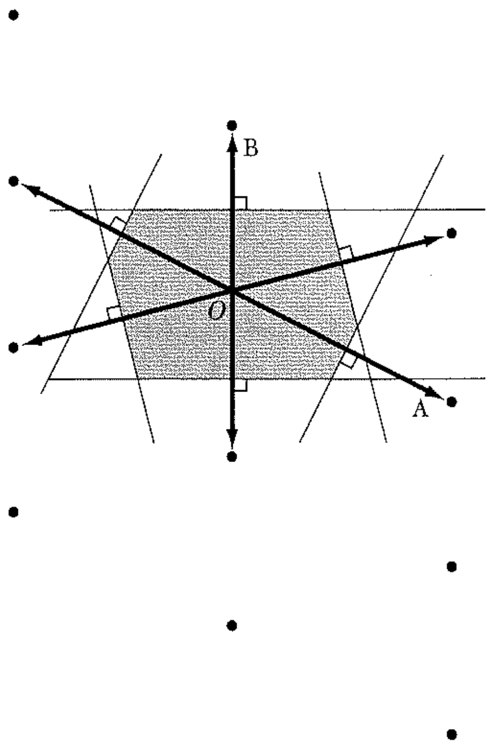


Figure 10 Construction of the first Brillouin zone for an oblique lattice in two dimensions. We first draw a number of vectors from O to nearby points in the reciprocal lattice. Next we construct lines perpendicular to these vectors at their midpoints. The smallest enclosed area is the first Brillouin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

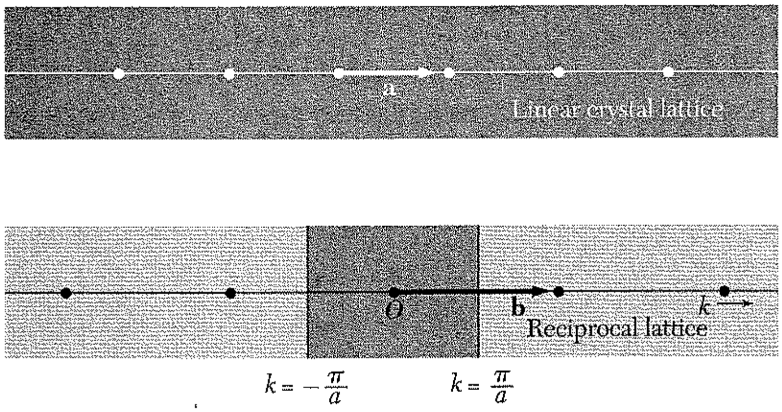


Figure 11 Crystal and reciprocal lattices in one dimension. The basis vector in the reciprocal lattice is **b**, of length equal to $2\pi/a$. The shortest reciprocal lattice vectors from the origin are **b** and $-$**b**. The perpendicular bisectors of these vectors form the boundaries of the first Brillouin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

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 $2\pi/a$.

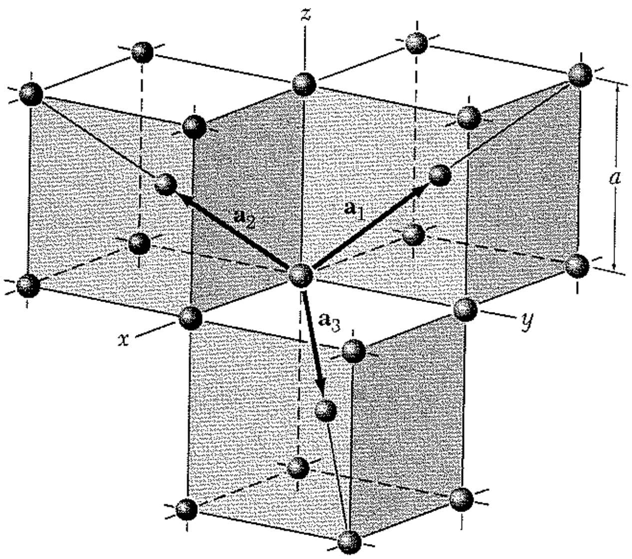


Figure 12 Primitive basis vectors of the body-centered cubic lattice.

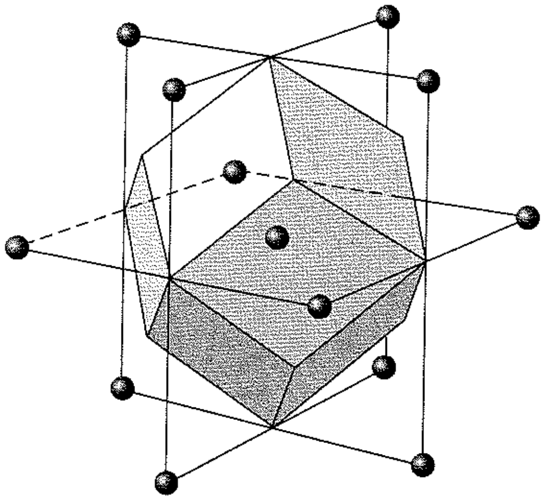


Figure 13 First Brillouin zone of the body-centered cubic lattice. The figure is a regular rhombic dodecahedron.

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:

$$\pm\tfrac{1}{2}\mathbf{b}_1 = \pm(\pi/a)\hat{\mathbf{x}} \ ; \qquad \pm\tfrac{1}{2}\mathbf{b}_2 = \pm(\pi/a)\hat{\mathbf{y}} \ ; \qquad \pm\tfrac{1}{2}\mathbf{b}_3 = \pm(\pi/a)\hat{\mathbf{z}} \ . \qquad (28)$$

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

$$\mathbf{a}_1 = \tfrac{1}{2}a(-\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}) \ ; \quad \mathbf{a}_2 = \tfrac{1}{2}a(\hat{\mathbf{x}} - \hat{\mathbf{y}} + \hat{\mathbf{z}}) \ ; \quad \mathbf{a}_3 = \tfrac{1}{2}a(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}}) \ , \qquad (29)$$

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

$$V = |\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3| = \tfrac{1}{2}a^3 \ . \qquad (30)$$

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

$$\mathbf{b}_1 = (2\pi/a)(\hat{\mathbf{y}} + \hat{\mathbf{z}}) \ ; \qquad \mathbf{b}_2 = (2\pi/a)(\hat{\mathbf{x}} + \hat{\mathbf{z}}) \ ; \qquad \mathbf{b}_3 = (2\pi/a)(\hat{\mathbf{x}} + \hat{\mathbf{y}}) \ . \quad (31)$$

Note by comparison with Fig. 14 (p. 37) 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,

$$\mathbf{G} = v_1\mathbf{b}_1 + v_2\mathbf{b}_2 + v_3\mathbf{b}_3 = (2\pi/a)[(v_2 + v_3)\hat{\mathbf{x}} + (v_1 + v_3)\hat{\mathbf{y}} + (v_1 + v_2)\hat{\mathbf{z}}] \ . \quad (32)$$

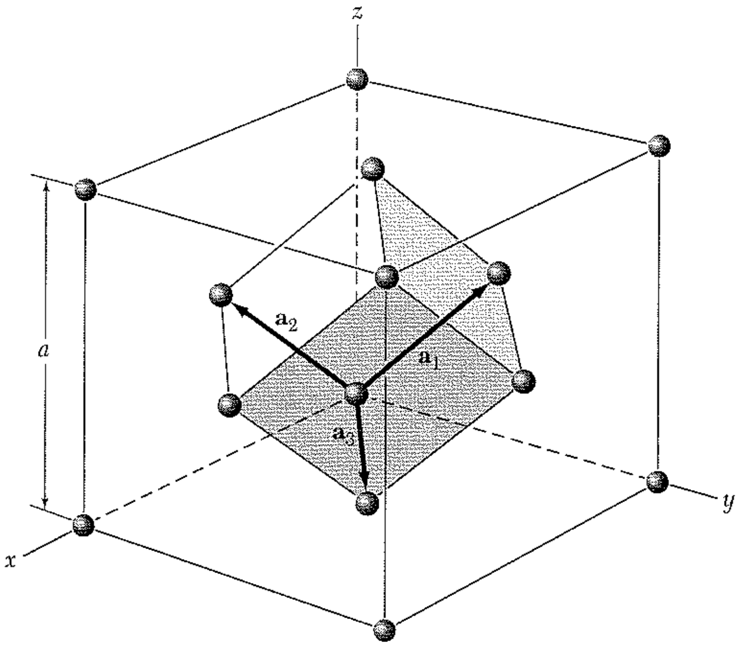


Figure 14 Primitive basis vectors of the face-centered cubic lattice.

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

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

One primitive cell of the reciprocal lattice is the parallelepiped described by the $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$ defined by (31). 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 (see Fig. 12).

Another primitive cell is the central (Wigner-Seitz) cell of the reciprocal lattice which is 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. (33) at their midpoints. The zone is a regular 12-faced solid, a rhombic dodecahedron, as shown in Fig. 13.

Reciprocal Lattice to fcc Lattice

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

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

The volume of the primitive cell is

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

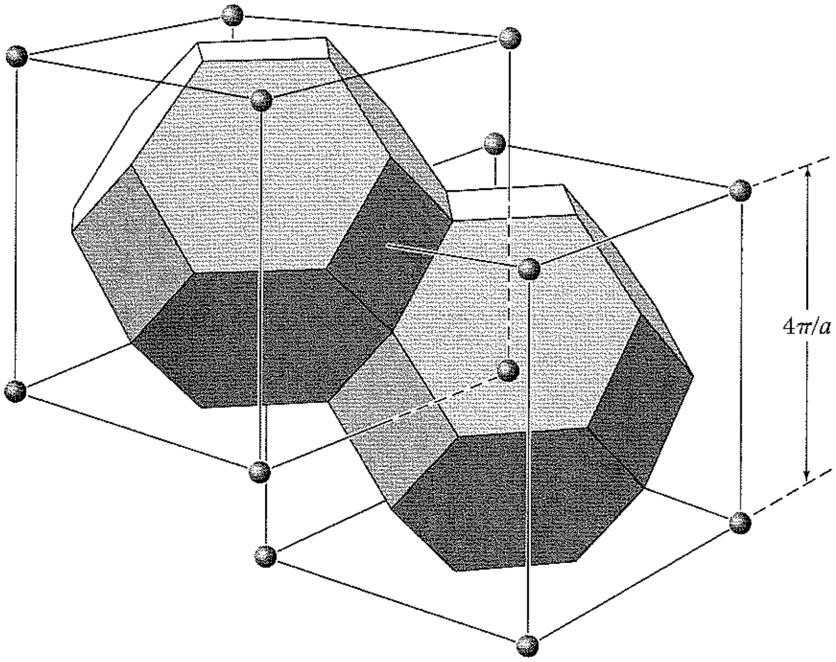


Figure 15 Brillouin zones of the face-centered cubic lattice. The cells are in reciprocal space, and the reciprocal lattice is body centered.

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

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

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 $(4\pi/a)^3$.

FOURIER ANALYSIS OF THE BASIS

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

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

The quantity $S_{\mathbf{G}}$ 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 single 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 density 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:

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

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

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

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 (1.2). Then, for the reflection labelled by v_1, v_2, v_3, we have

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

so that (43) becomes

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

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.

Structure 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

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

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

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

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 is the physical interpretation of the result that the (100) reflection vanishes? The (100) reflection normally occurs when reflections from the planes that bound the cubic cell differ in phase by 2π. In the bcc lattice there is an intervening plane (Fig. 16) of atoms, labeled the second plane in the figure, which is equal in scattering power to the other planes. Situated midway between them, it gives a reflection retarded in phase by π with respect to the first plane, thereby canceling the contribution from that plane. The cancellation of the (100) reflection occurs in the bcc lattice because the planes are identical in composition. A similar cancellation can easily be found in the hcp structure.

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

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

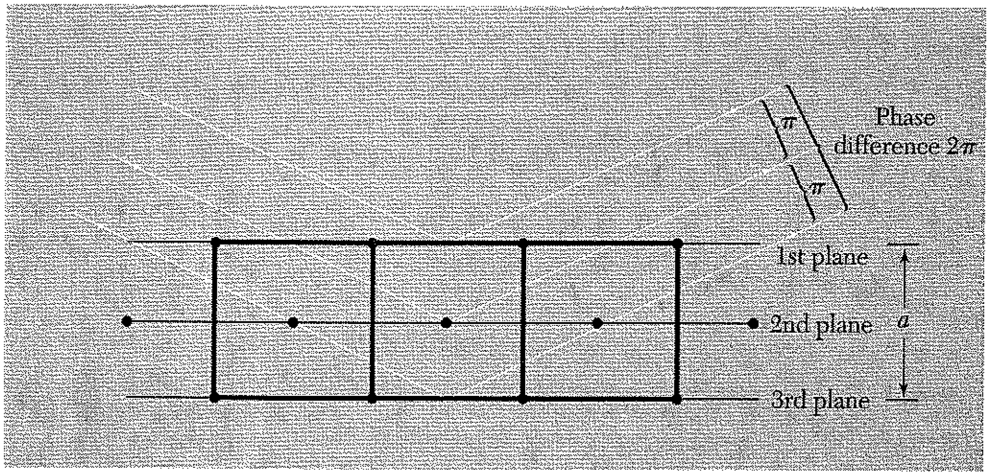


Figure 16 Explanation of the absence of a (100) reflection from a body-centered cubic lattice. The phase difference between successive planes is π, so that the reflected amplitude from two adjacent planes is $1 + e^{-i\pi} = 1 - 1 = 0$.

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.

The point is beautifully illustrated by Fig. 17: both KCl and KBr have an fcc lattice, but $n(\mathbf{r})$ for KCl simulates an sc lattice because the K^+ and Cl^- ions have equal numbers of electrons.

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

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

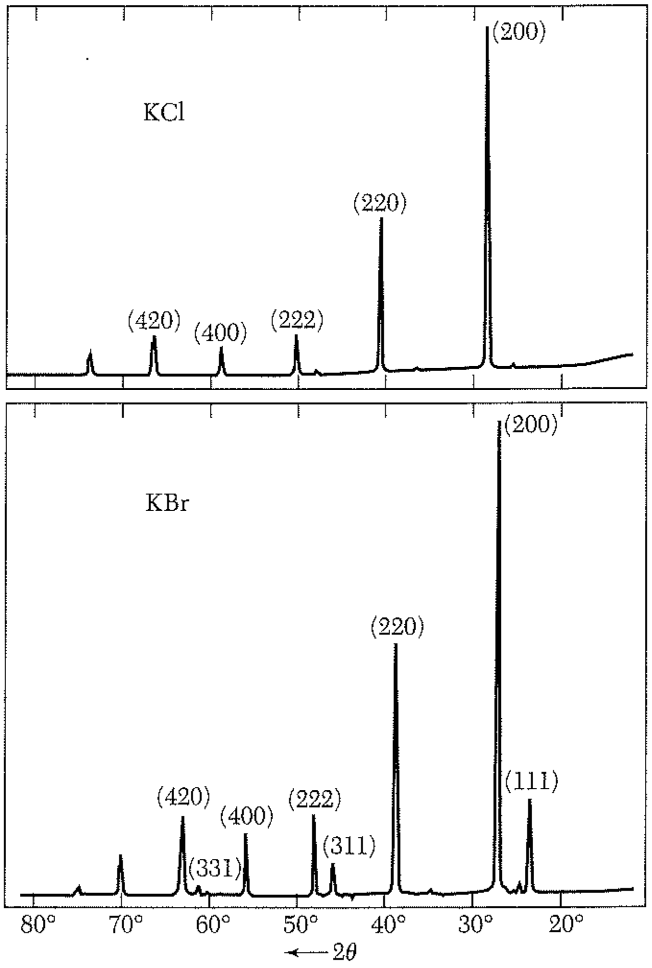


Figure 17 Comparison of x-ray reflections from KCl and KBr powders. In KCl the numbers of electrons of K^+ and Cl^- ions are equal. The scattering amplitudes $f(K^+)$ and $f(Cl^-)$ are almost exactly equal, so that the crystal looks to x-rays as if it were a monatomic simple cubic lattice of lattice 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 to that of K^+, and all reflections of the fcc lattice are present. (Courtesy of R. van Nordstrand.)

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

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

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 somewhat 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.

SUMMARY

- Various statements of the Bragg condition:

$$2d \sin\theta = n\lambda \ ; \qquad \Delta\mathbf{k} = \mathbf{G} \ ; \qquad 2\mathbf{k}\cdot\mathbf{G} = G^2 \ .$$

- Laue conditions:

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

- The primitive translation vectors of the reciprocal lattice are

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

  Here $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ are the primitive translation vectors of the crystal lattice.

- A reciprocal lattice vector has the form

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

  where v_1, v_2, v_3 are integers or zero.

- The scattered amplitude in the direction $\mathbf{k}' = \mathbf{k} + \Delta\mathbf{k} = \mathbf{k} + \mathbf{G}$ is proportional to the geometrical structure factor:

$$S_{\mathbf{G}} \equiv \sum f_j \exp(-i\mathbf{r}_j\cdot\mathbf{G}) = \sum f_j \exp[-i2\pi(x_j v_1 + y_j v_2 + z_j v_3)] \ ,$$

  where j runs over the s atoms of the basis, and f_j is the atomic form factor (49) of the jth atom of the basis. The expression on the right-hand side is written for a reflection $(v_1v_2v_3)$, for which $\mathbf{G} = v_1\mathbf{b}_1 + v_2\mathbf{b}_2 + v_3\mathbf{b}_3$.

- Any function invariant under a lattice translation $\mathbf{T}$ may be expanded in a Fourier series of the form

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

- The first Brillouin zone is the Wigner-Seitz primitive cell of the reciprocal lattice. Only waves whose wavevector **k** drawn from the origin terminates on a surface of the Brillouin zone can be diffracted by the crystal.

Crystal lattice	*First Brillouin zone*
Simple cubic	Cube
Body-centered cubic	Rhombic dodecahedron (Fig. 13)
Face-centered cubic	Truncated octahedron (Fig. 15)

Problems

1. ***Interplanar separation.*** Consider a plane *hkl* in a crystal lattice. (a) Prove that the reciprocal lattice vector $\mathbf{G} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$ is perpendicular to this plane. (b) Prove that the distance between two adjacent parallel planes of the lattice is $d(hkl) = 2\pi/|\mathbf{G}|$. (c) Show for a simple cubic lattice that $d^2 = a^2/(h^2 + k^2 + l^2)$.

2. ***Hexagonal space lattice.*** The primitive translation vectors of the hexagonal space lattice may be taken as

$$\mathbf{a}_1 = (3^{1/2}a/2)\hat{\mathbf{x}} + (a/2)\hat{\mathbf{y}} \ ; \qquad \mathbf{a}_2 = -(3^{1/2}a/2)\hat{\mathbf{x}} + (a/2)\hat{\mathbf{y}} \ ; \qquad \mathbf{a}_3 = c\hat{\mathbf{z}} \ .$$

(a) Show that the volume of the primitive cell is $(3^{1/2}/2)a^2c$.
(b) Show that the primitive translations of the reciprocal lattice are

$$\mathbf{b}_1 = (2\pi/3^{1/2}a)\hat{\mathbf{x}} + (2\pi/a)\hat{\mathbf{y}} \ ; \qquad \mathbf{b}_2 = -(2\pi/3^{1/2}a)\hat{\mathbf{x}} + (2\pi/a)\hat{\mathbf{y}} \ ; \qquad \mathbf{b}_3 = (2\pi/c)\hat{\mathbf{z}} \ ,$$

so that the lattice is its own reciprocal, but with a rotation of axes.
(c) Describe and sketch the first Brillouin zone of the hexagonal space lattice.

3. ***Volume of Brillouin zone.*** Show that the volume of the first Brillouin zone is $(2\pi)^3/V_c$, where V_c is the volume of a crystal primitive cell. Hint: The volume of a Brillouin zone is equal to the volume of the primitive parallelepiped in Fourier space. Recall the vector identity $(\mathbf{c} \times \mathbf{a}) \times (\mathbf{a} \times \mathbf{b}) = (\mathbf{c} \cdot \mathbf{a} \times \mathbf{b})\mathbf{a}$.

4. ***Width of diffraction maximum.*** We suppose that in a linear crystal there are identical point scattering centers at every lattice point $\boldsymbol{\rho}_m = m\mathbf{a}$, where m is an integer. By analogy with (20), the total scattered radiation amplitude will be proportional to $F = \Sigma \exp[-im\mathbf{a} \cdot \Delta\mathbf{k}]$. The sum over M lattice points is

$$F = \frac{1 - \exp[-iM(\mathbf{a} \cdot \Delta\mathbf{k}]}{1 - \exp[-i(\mathbf{a} \cdot \Delta\mathbf{k})]} \ ,$$

by the use of the series

$$\sum_{m=0}^{M-1} x^m = \frac{1 - x^M}{1 - x} \ .$$

(a) The scattered intensity is proportional to $|F|^2$. Show that

$$|F|^2 \equiv F^*F = \frac{\sin^2 \frac{1}{2} M(\mathbf{a} \cdot \Delta\mathbf{k})}{\sin^2 \frac{1}{2} (\mathbf{a} \cdot \Delta\mathbf{k})} \ .$$

(b) We know that a diffraction maximum appears when $\mathbf{a} \cdot \Delta\mathbf{k} = 2\pi h$, where h is an integer. We change $\Delta\mathbf{k}$ slightly and define ϵ in $\mathbf{a} \cdot \Delta\mathbf{k} = 2\pi h + \epsilon$ such that ϵ gives the position of the first zero in $\sin \frac{1}{2}M(\mathbf{a} \cdot \Delta\mathbf{k})$. Show that $\epsilon = 2\pi/M$, so that the width of the diffraction maximum is proportional to $1/M$ and can be extremely narrow for macroscopic values of M. The same result holds true for a three-dimensional crystal.

5. ***Structure factor of diamond.*** The crystal structure of diamond is described in Chapter 1. The basis consists of eight atoms if the cell is taken as the conventional cube. (a) Find the structure factor S of this basis. (b) Find the zeros of S and show that the allowed reflections of the diamond structure satisfy $v_1 + v_2 + v_3 = 4n$, where all indices are even and n is any integer, or else all indices are odd (Fig. 18). (Notice that h, k, l may be written for v_1, v_2, v_3 and this is often done.)

6. ***Form factor of atomic hydrogen.*** For the hydrogen atom in its ground state, the number density is $n(r) = (\pi a_0^3)^{-1} \exp(-2r/a_0)$, where a_0 is the Bohr radius. Show that the form factor is $f_G = 16/(4 + G^2a_0^2)^2$.

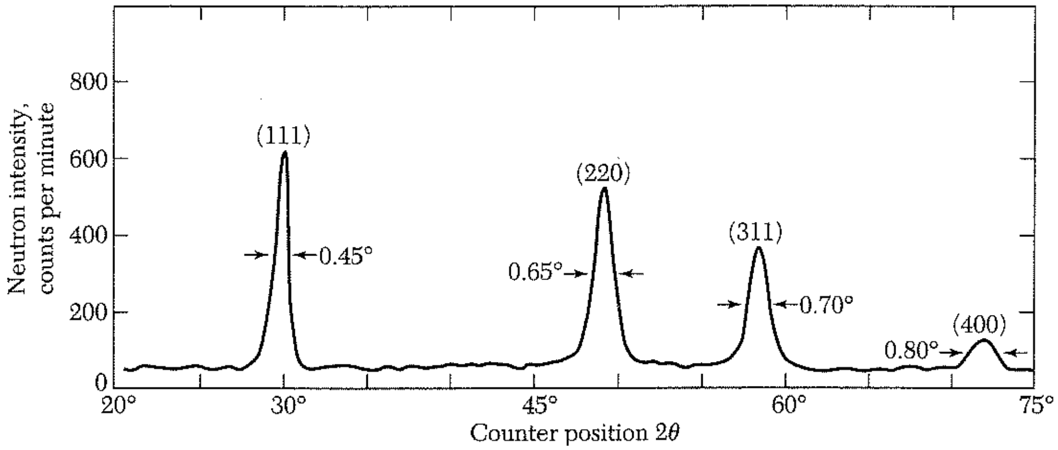


Figure 18 Neutron diffraction pattern for powdered diamond. (After G. Bacon.)

7. ***Diatomic line.*** Consider a line of atoms *ABAB . . . AB*, with an *A*—*B* bond length of $\frac{1}{2}a$. The form factors are f_A, f_B for atoms *A*, *B*, respectively. The incident beam of x-rays is perpendicular to the line of atoms. (a) Show that the interference condition is $n\lambda = a\cos\theta$, where θ is the angle between the diffracted beam and the line of atoms. (b) Show that the intensity of the diffracted beam is proportional to $|f_A - f_B|^2$ for n odd, and to $|f_A + f_B|^2$ for n even. (c) Explain what happens if $f_A = f_B$.

$\sin^2 a = \frac{1}{2}(1-\cos 2a)$

7

Energy Bands

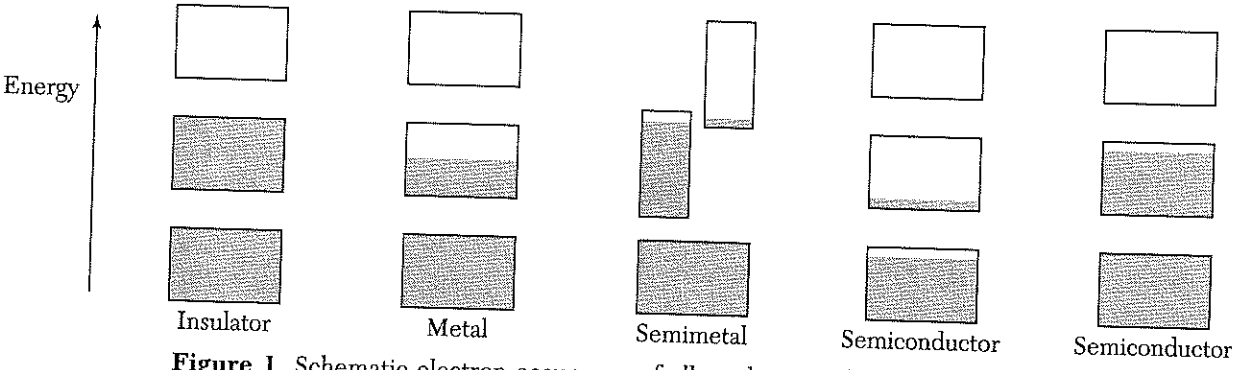


Figure 1 Schematic electron occupancy of allowed energy bands for an insulator, metal, semimetal, and semiconductor. The vertical extent of the boxes indicates the allowed energy regions; the shaded areas indicate the regions filled with electrons. In a **semimetal** (such as bismuth) one band is almost filled and another band is nearly empty at absolute zero, but a pure **semiconductor** (such as silicon) becomes an insulator at absolute zero. The left of the two semiconductors shown is at a finite temperature, with carriers excited thermally. The other semiconductor is electron-deficient because of impurities.

CHAPTER 7: ENERGY BANDS

> ***When I started to think about it, I felt that the main problem was to explain how the electrons could sneak by all the ions in a metal. . . . By straight Fourier analysis I found to my delight that the wave differed from the plane wave of free electrons only by a periodic modulation.***
>
> F. Bloch

The free electron model of metals gives us good insight into the heat capacity, thermal conductivity, electrical conductivity, magnetic susceptibility, and electrodynamics of metals. But the model fails to help us with other large questions: the distinction between metals, semimetals, semiconductors, and insulators; the occurrence of positive values of the Hall coefficient; the relation of conduction electrons in the metal to the valence electrons of free atoms; and many transport properties, particularly magnetotransport. We need a less naïve theory, and fortunately it turns out that almost any simple attempt to improve upon the free electron model is enormously profitable.

The difference between a good conductor and a good insulator is striking. The electrical resistivity of a pure metal may be as low as 10^{-10} ohm-cm at a temperature of 1 K, apart from the possibility of superconductivity. The resistivity of a good insulator may be as high as 10^{22} ohm-cm. This range of 10^{32} may be the widest of any common physical property of solids.

Every solid contains electrons. The important question for electrical conductivity is how the electrons respond to an applied electric field. We shall see that electrons in crystals are arranged in **energy bands** (Fig. 1) separated by regions in energy for which no wavelike electron orbitals exist. Such forbidden regions are called **energy gaps** or **band gaps**, and result from the interaction of the conduction electron waves with the ion cores of the crystal.

The crystal behaves as an insulator if the allowed energy bands are either filled or empty, for then no electrons can move in an electric field. The crystal behaves as a metal if one or more bands are partly filled, say between 10 and 90 percent filled. The crystal is a semiconductor or a semimetal if one or two bands are slightly filled or slightly empty.

To understand the difference between insulators and conductors, we must extend the free electron model to take account of the periodic lattice of the solid. The possibility of a band gap is the most important new property that emerges.

We shall encounter other quite remarkable properties of electrons in crystals. For example, they respond to applied electric or magnetic fields as if the electrons were endowed with an effective mass m^*, which may be larger or smaller than the free electron mass, or may even be negative. Electrons in crystals respond to applied fields as if endowed with negative or positive charges, $-e$ or $+e$, and herein lies the explanation of the negative and positive values of the Hall coefficient.

NEARLY FREE ELECTRON MODEL

On the free electron model the allowed energy values are distributed essentially continuously from zero to infinity. We saw in Chapter 6 that

$$\epsilon_{\mathbf{k}} = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2) \ , \tag{1}$$

where, for periodic boundary conditions over a cube of side L,

$$k_x, k_y, k_z = 0 \ ; \quad \pm\frac{2\pi}{L} \ ; \quad \pm\frac{4\pi}{L} \ ; \ \ldots \ . \tag{2}$$

The free electron wavefunctions are of the form

$$\psi_{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k}\cdot\mathbf{r}) \ ; \tag{3}$$

they represent running waves and carry momentum $\mathbf{p} = \hbar\mathbf{k}$.

The band structure of a crystal can often be explained by the nearly free electron model for which the band electrons are treated as perturbed only weakly by the periodic potential of the ion cores. This model answers almost all the qualitative questions about the behavior of electrons in metals.

We know that Bragg reflection is a characteristic feature of wave propagation in crystals. Bragg reflection of electron waves in crystals is the cause of energy gaps. (At Bragg reflection wavelike solutions of the Schrödinger equation do not exist, as in Fig. 2.) These energy gaps are of decisive significance in determining whether a solid is an insulator or a conductor.

We explain physically the origin of energy gaps in the simple problem of a linear solid of lattice constant a. The low energy portions of the band structure

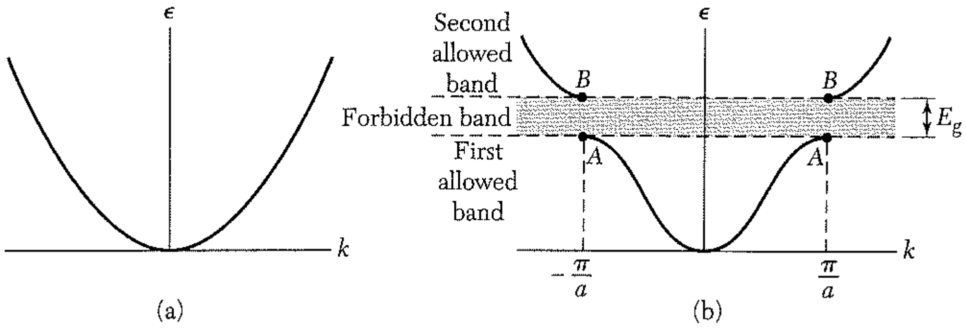


Figure 2 (a) Plot of energy ϵ versus wavevector k for a free electron. (b) Plot of energy versus wavevector for an electron in a monatomic linear lattice of lattice constant a. The energy gap E_g shown is associated with the first Bragg reflection at $k = \pm\pi/a$; other gaps are found at higher energies at $\pm n\pi/a$, for integral values of n.

are shown qualitatively in Fig. 2, in (a) for entirely free electrons and in (b) for electrons that are nearly free, but with an energy gap at $k = \pm\pi/a$. The Bragg condition $(\mathbf{k} + \mathbf{G})^2 = k^2$ for diffraction of a wave of wavevector $\mathbf{k}$ becomes in one dimension

$$k = \pm\tfrac{1}{2}G = \pm n\pi/a \ , \tag{4}$$

where $G = 2\pi n/a$ is a reciprocal lattice vector and n is an integer. The first reflections and the first energy gap occur at $k = \pm\pi/a$. The region in $\mathbf{k}$ space between $-\pi/a$ and π/a is the **first Brillouin zone** of this lattice. Other energy gaps occur for other values of the integer n.

The wavefunctions at $k = \pm\pi/a$ are not the traveling waves $\exp(i\pi x/a)$ or $\exp(-i\pi x/a)$ of free electrons. At these special values of k the wavefunctions are made up of equal parts of waves traveling to the right and to the left. When the Bragg reflection condition $k = \pm\pi/a$ is satisfied by the wavevector, a wave traveling to the right is Bragg-reflected to travel to the left, and vice versa. Each subsequent Bragg reflection will reverse the direction of travel of the wave. A wave that travels neither to the right nor to the left is a standing wave: it doesn't go anywhere.

The time-independent state is represented by standing waves. We can form two different standing waves from the two traveling waves

$$\exp(\pm\, i\pi x/a) = \cos(\pi x/a) \pm i \sin(\pi x/a),$$

so that the standing waves are

$$\begin{aligned} \psi(+) &= \exp(i\pi x/a) + \exp(-i\pi x/a) = 2\cos(\pi x/a) \ ; \\ \psi(-) &= \exp(i\pi x/a) - \exp(-i\pi x/a) = 2i\sin(\pi x/a) \ . \end{aligned} \tag{5}$$

The standing waves are labeled $(+)$ or $(-)$ according to whether or not they change sign when $-x$ is substituted for x. Both standing waves are composed of equal parts of right- and left-directed traveling waves.

Origin of the Energy Gap

The two standing waves $\psi(+)$ and $\psi(-)$ pile up electrons at different regions, and therefore the two waves have different values of the potential energy in the field of the ions of the lattice. This is the origin of the energy gap. The probability density ρ of a particle is $\psi^*\psi = |\psi|^2$. For a pure traveling wave $\exp(ikx)$, we have $\rho = \exp(-ikx)\exp(ikx) = 1$, so that the charge density is constant. The charge density is not constant for linear combinations of plane waves. Consider the standing wave $\psi(+)$ in (5); for this we have

$$\rho(+) = |\psi(+)|^2 \propto \cos^2 \pi x/a \ .$$

This function piles up electrons (negative charge) on the positive ions centered at $x = 0, a, 2a, \ldots$ in Fig. 3, where the potential energy is lowest.

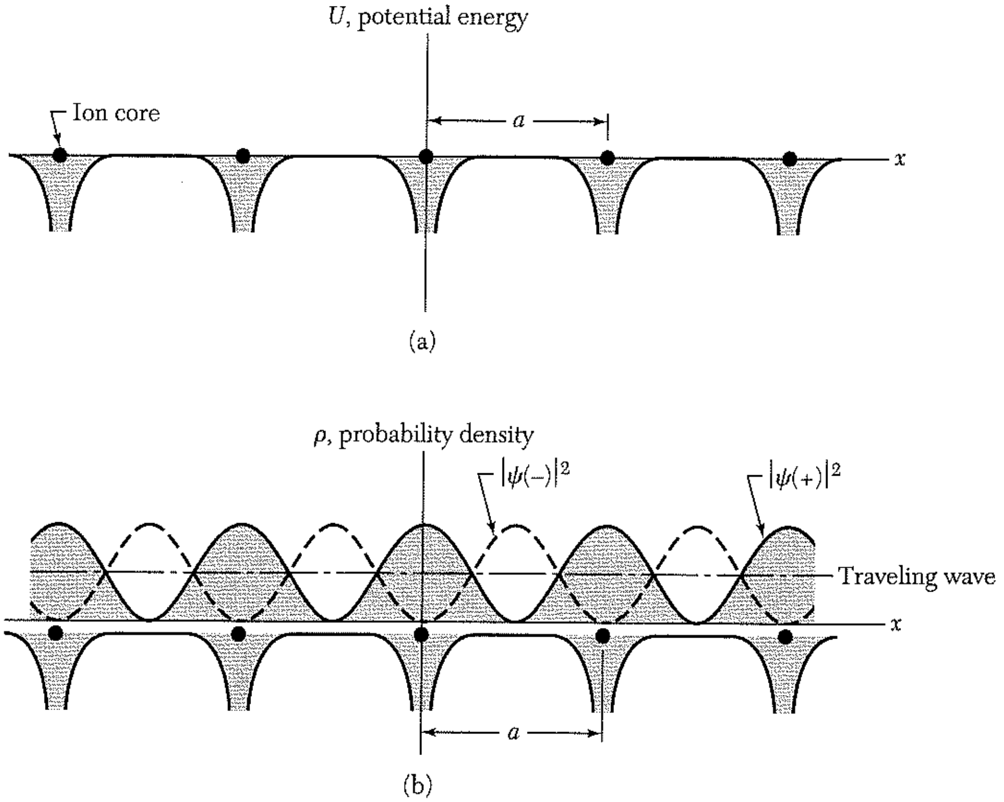


Figure 3 (a) Variation of potential energy of a conduction electron in the field of the ion cores of a linear lattice. (b) Distribution of probability density ρ in the lattice for $|\psi(-)|^2 \propto \sin^2 \pi x/a$; $|\psi(+)|^2 \propto \cos^2 \pi x/a$; and for a traveling wave. The wavefunction $\psi(+)$ piles up electronic charge on the cores of the positive ions, thereby lowering the potential energy in comparison with the average potential energy seen by a traveling wave. The wavefunction $\psi(-)$ piles up charge in the region between the ions, thereby raising the potential energy in comparison with that seen by a traveling wave. This figure is the key to understanding the origin of the energy gap.

Figure 3a pictures the variation of the electrostatic potential energy of a conduction electron in the field of the positive ion cores. The ion cores bear a net positive charge because the atoms are ionized in the metal, with the valence electrons taken off to form the conduction band. The potential energy of an electron in the field of a positive ion is negative, so that the force between them is attractive.

For the other standing wave $\psi(-)$ the probability density is

$$\rho(-) = |\psi(-)|^2 \propto \sin^2 \pi x/a \ ,$$

which concentrates electrons away from the ion cores. In Fig. 3b we show the electron concentration for the standing waves $\psi(+)$, $\psi(-)$, and for a traveling wave.

When we calculate the average or expectation values of the potential energy over these three charge distributions, we find that the potential energy of $\rho(+)$ is lower than that of the traveling wave, whereas the potential energy of $\rho(-)$ is higher than the traveling wave. We have an energy gap of width E_g if the energies of $\rho(-)$ and $\rho(+)$ differ by E_g. Just below the energy gap at points A in Fig. 2 the wavefunction is $\psi(+)$, and just above the gap at points B the wavefunction is $\psi(-)$.

Magnitude of the Energy Gap

The wavefunctions at the Brillouin zone boundary $k = \pi/a$ are $\sqrt{2}\cos \pi x/a$ and $\sqrt{2}\sin \pi x/a$, normalized over unit length of line. Let us suppose that the potential energy of an electron in the crystal at point x is

$$U(x) = U\cos 2\pi x/a \ .$$

The first-order energy difference between the two standing wave states is

$$\begin{aligned} E_g &= \int_0^1 dx\, U(x)\,[|\psi(+)|^2 - |\psi(-)|^2] \\ &= 2\int dx\, U\cos(2\pi x/a)(\cos^2 \pi x/a - \sin^2 \pi x/a) = U \ . \end{aligned} \tag{6}$$

We see that the gap is equal to the Fourier component of the crystal potential.

BLOCH FUNCTIONS

F. Bloch proved the important theorem that the solutions of the Schrödinger equation for a periodic potential must be of a special form:

$$\boxed{\psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r})\exp(i\mathbf{k}\cdot\mathbf{r}) \ ,} \tag{7}$$

where $u_{\mathbf{k}}(\mathbf{r})$ has the period of the crystal lattice with $u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{T})$. Here $\mathbf{T}$ is a translation vector of the lattice. The result (7) expresses the Bloch theorem:

> The eigenfunctions of the wave equation for a periodic potential are the product of a plane wave $\exp(i\mathbf{k}\cdot\mathbf{r})$ times a function $u_{\mathbf{k}}(\mathbf{r})$ with the periodicity of the crystal lattice.

A one-electron wavefunction of the form (7) is called a Bloch function and can be decomposed into a sum of traveling waves, as we see later. Bloch functions can be assembled into wave packets to represent electrons that propagate freely through the potential field of the ion cores.

We give now a restricted proof of the Bloch theorem, valid when ψ_k is nondegenerate; that is, when there is no other wavefunction with the same energy and wavevector as ψ_k. The general case will be treated later. We consider N identical lattice points on a ring of length Na. The potential energy is periodic in a, with $U(x) = U(x + sa)$, where s is an integer.

Let us be guided by the symmetry of the ring to look for solutions of the wave equation such that

$$\psi(x + a) = C\psi(x) \ , \tag{8}$$

where C is a constant. Then, on going once around the ring,

$$\psi(x + Na) = \psi(x) = C^N \psi(x) \ ,$$

because $\psi(x)$ must be single-valued. It follows that C is one of the N roots of unity, or

$$C = \exp(i2\pi s/N) \ ; \qquad s = 0, 1, 2, \ . \ . \ . \ , N - 1 \ . \tag{9}$$

We use (9) to see that

$$\psi(x) = u_k(x) \exp(i2\pi sx/Na) \tag{10}$$

satisfies (8), provided that $u_k(x)$ has the periodicity a, so that $u_k(x) = u_k(x + a)$. This is the Bloch result (7).

KRONIG-PENNEY MODEL

A periodic potential for which the wave equation can be solved in terms of elementary functions is the square-well array of Fig. 4. The wave equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + U(x)\psi = \epsilon\psi \ , \tag{11}$$

where $U(x)$ is the potential energy and ϵ is the energy eigenvalue.

In the region $0 < x < a$ in which $U = 0$, the eigenfunction is a linear combination,

$$\psi = Ae^{iKx} + Be^{-iKx} \ , \tag{12}$$

of plane waves traveling to the right and to the left, with energy

$$\epsilon = \hbar^2K^2/2m \ . \tag{13}$$

In the region $-b < x < 0$ within the barrier the solution is of the form

$$\psi = Ce^{Qx} + De^{-Qx} \ , \tag{14}$$

with

$$U_0 - \epsilon = \hbar^2Q^2/2m \ . \tag{15}$$

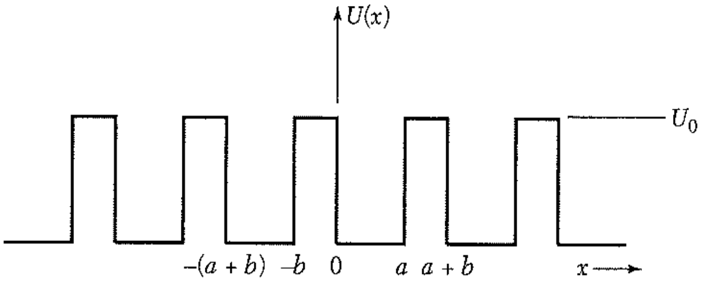


Figure 4 Square-well periodic potential as introduced by Kronig and Penney.

We want the complete solution to have the Bloch form (7). Thus the solution in the region $a < x < a + b$ must be related to the solution (14) in the region $-b < x < 0$ by the Bloch theorem:

$$\psi(a < x < a + b) = \psi(-b < x < 0)\, e^{ik(a+b)} \ , \tag{16}$$

which serves to define the wavevector k used as an index to label the solution.

The constants A, B, C, D are chosen so that ψ and $d\psi/dx$ are continuous at $x = 0$ and $x = a$. These are the usual quantum mechanical boundary conditions in problems that involve square potential wells. At $x = 0$,

$$A + B = C + D \ ; \tag{17}$$

$$iK(A - B) = Q(C - D) \ , \tag{18}$$

with Q from (14). At $x = a$, with the use of (16) for $\psi(a)$ under the barrier in terms of $\psi(-b)$,

$$Ae^{iKa} + Be^{-iKa} = (Ce^{-Qb} + De^{Qb})\, e^{ik(a+b)} \ ; \tag{19}$$

$$iK(Ae^{iKa} - Be^{-iKa}) = Q(Ce^{-Qb} - De^{Qb})\, e^{ik(a+b)} \ . \tag{20}$$

The four equations (17) to (20) have a solution only if the determinant of the coefficients of A, B, C, D vanishes, yielding

$$[(Q^2 - K^2)/2QK] \sinh Qb \sin Ka + \cosh Qb \cos Ka = \cos k(a + b) \ . \tag{21a}$$

It is rather tedious to obtain this equation.

The result is simplified if we represent the potential by the periodic delta function obtained when we pass to the limit $b = 0$ and $U_0 = \infty$ in such a way that $Q^2ba/2 = P$, a finite quantity. In this limit $Q \gg K$ and $Qb \ll 1$. Then (21a) reduces to

$$(P/Ka)\sin Ka + \cos Ka = \cos ka \ . \tag{21b}$$

The ranges of K for which this equation has solutions are plotted in Fig. 5, for the case $P = 3\pi/2$. The corresponding values of the energy are plotted in Fig. 6. Note the energy gaps at the zone boundaries. The wavevector k of the Bloch function is the important index, not the K in (12), which is related to the energy by (13). A treatment of this problem in wavevector space is given later in this chapter.

WAVE EQUATION OF ELECTRON IN A PERIODIC POTENTIAL

We considered in Fig. 3 the approximate form we expect for the solution of the Schrödinger equation if the wavevector is at a zone boundary, as at $k = \pm\pi/a$. We treat in detail the wave equation for a general potential, at general

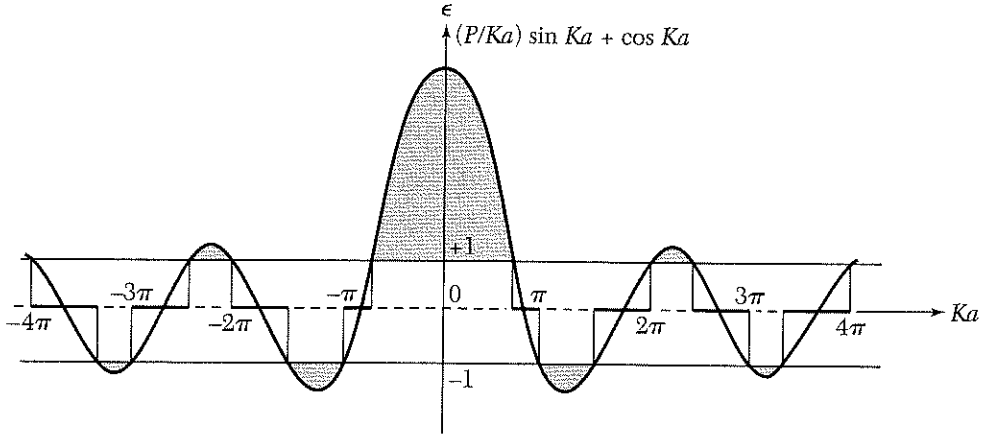


Figure 5 Plot of the function $(P/Ka)\sin Ka + \cos Ka$, for $P = 3\pi/2$. The allowed values of the energy e are given by those ranges of $Ka = (2m\epsilon/\hbar^2)^{1/2}a$ for which the function lies between ± 1. For other values of the energy there are no traveling wave or Bloch-like solutions to the wave equation, so that forbidden gaps in the energy spectrum are formed.

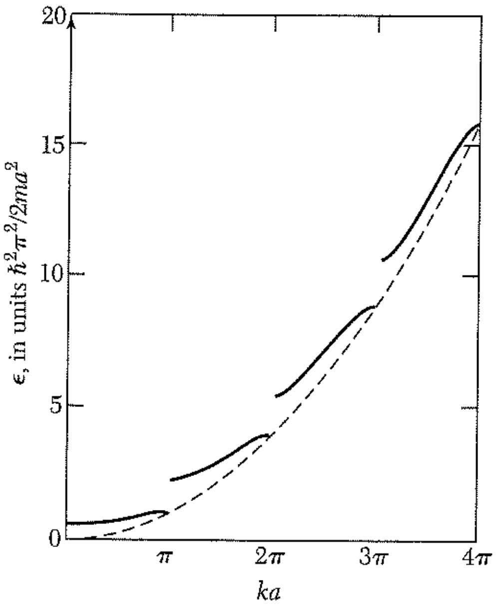


Figure 6 Plot of energy vs. wavenumber for the Kronig-Penney potential, with $P = 3\pi/2$. Notice the energy gaps at $ka = \pi, 2\pi, 3\pi \ldots$.

values of k. Let $U(x)$ denote the potential energy of an electron in a linear lattice of lattice constant a. We know that the potential energy is invariant under a crystal lattice translation: $U(x) = U(x + a)$. A function invariant under a crystal lattice translation may be expanded as a Fourier series in the reciprocal lattice vectors G. We write the Fourier series for the potential energy as

$$U(x) = \sum_G U_G e^{iGx} \ . \tag{22}$$

The values of the coefficients U_G for actual crystal potentials tend to decrease rapidly with increasing magnitude of G. For a bare coulomb potential U_G decreases as $1/G^2$.

We want the potential energy $U(x)$ to be a real function:

$$U(x) = \sum_{G>0} U_G(e^{iGx} + e^{-iGx}) = 2\sum_{G>0} U_G \cos Gx \ . \tag{23}$$

For convenience we have assumed that the crystal is symmetric about $x = 0$ and that $U_0 = 0$.

The wave equation of an electron in the crystal is $\mathcal{H}\psi = \epsilon\psi$, where $\mathcal{H}$ is the hamiltonian and ϵ is the energy eigenvalue. The solutions ψ are called eigenfunctions or orbitals or Bloch functions. Explicitly, the wave equation is

$$\left(\frac{1}{2m}p^2 + U(x)\right)\psi(x) = \left(\frac{1}{2m}p^2 + \sum_G U_G\, e^{iGx}\right)\psi(x) = \epsilon\psi(x) \ . \tag{24}$$

Equation (24) is written in the one-electron approximation in which the orbital $\psi(x)$ describes the motion of one electron in the potential of the ion cores and in the average potential of the other conduction electrons.

The wavefunction $\psi(x)$ may be expressed as a Fourier series summed over all values of the wavevector permitted by the boundary conditions, so that

$$\psi = \sum_k C(k)\, e^{ikx} \ , \tag{25}$$

where k is real. (We could equally well write the index k as a subscript on C, as in C_k.)

The set of values of k has the form $2\pi n/L$, because these values satisfy periodic boundary conditions over length L. Here n is any integer, positive or negative. We do not assume, nor is it generally true, that $\psi(x)$ itself is periodic in the fundamental lattice translation a. The translational properties of $\psi(x)$ are determined by the Bloch theorem (7).

Not all wavevectors of the set $2\pi n/L$ enter the Fourier expansion of any one Bloch function. If one particular wavevector k is contained in a ψ, then all other wavevectors in the Fourier expansion of this ψ will have the form $k + G$, where G is any reciprocal lattice vector. We prove this result in (29) below.

We can label a wavefunction ψ that contains a component k as ψ_k or, equally well, as ψ_{k+G}, because if k enters the Fourier expansion then $k + G$ may enter. The wavevectors $k + G$ running over G are a restricted subset of the set $2\pi n/L$, as shown in Fig. 7.

We shall usually choose as a label for the Bloch function that k which lies within the first Brillouin zone. When other conventions are used, we shall say so. This situation differs from the phonon problem for a monatomic lattice where there are no components of the ion motion outside the first zone. The electron problem is like the x-ray diffraction problem because like the electron wavefunction the electromagnetic field exists everywhere within the crystal and not only at the ions.

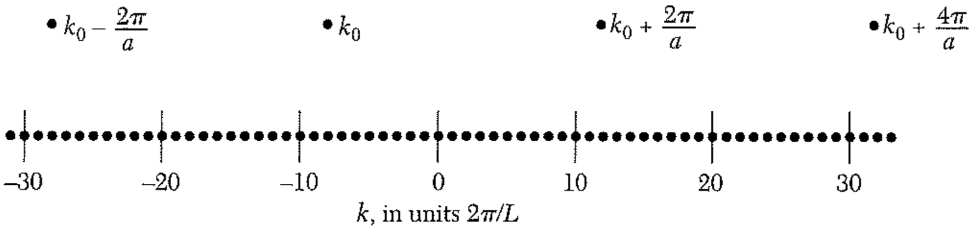


Figure 7 The lower points represent values of the wavevector $k = 2\pi n/L$ allowed by the periodic boundary condition on the wavefunction over a ring of circumference L composed of 20 primitive cells. The allowed values continue to $\pm\infty$. The upper points represent the first few wavevectors which may enter into the Fourier expansion of a wavefunction $\psi(x)$, starting from a particular wavevector $k = k_0 = -8(2\pi/L)$. The shortest reciprocal lattice vector is $2\pi/a = 20(2\pi/L)$.

To solve the wave equation, substitute (25) in (24) to obtain a set of linear algebraic equations for the Fourier coefficients. The kinetic energy term is

$$\frac{1}{2m}p^2\psi(x) = \frac{1}{2m}\left(-i\hbar\frac{d}{dx}\right)^2\psi(x) = -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = \frac{\hbar^2}{2m}\sum_k k^2 C(k)\,e^{ikx} \;;$$

and the potential energy term is

$$\left(\sum_G U_G e^{iGx}\right)\psi(x) = \sum_G\sum_k U_G e^{iGx} C(k)\,e^{ikx} \;.$$

The wave equation is obtained as the sum:

$$\sum_k \frac{\hbar^2}{2m}k^2 C(k)\,e^{ikx} + \sum_G\sum_k U_G C(k)\,e^{i(k+G)x} = \epsilon\sum_k C(k)\,e^{ikx} \;. \tag{26}$$

Each Fourier component must have the same coefficient on both sides of the equation. Thus we have the **central equation**

$$\boxed{(\lambda_k - \epsilon)C(k) + \sum_G U_G C(k-G) = 0 \;.} \tag{27}$$

with the notation

$$\lambda_k = \hbar^2 k^2/2m \;. \tag{28}$$

Equation (27) is a useful form of the wave equation in a periodic lattice, although unfamiliar because a set of algebraic equations has taken the place of the usual differential equation (24). The set appears unpleasant and formidable because there are, in principle, an infinite number of $C(k - G)$ to be determined. In practice a small number will often suffice, perhaps two or four. It takes some experience to appreciate the practical advantages of the algebraic approach.

Restatement of the Bloch Theorem

Once we determine the C's from (27), the wavefunction (25) is given as

$$\psi_k(x) = \sum_G C(k-G)\, e^{i(k-G)x} \ , \tag{29}$$

which may be rearranged as

$$\psi_k(x) = \left(\sum_G C(k-G)\, e^{-iGx} \right) e^{ikx} = e^{ikx} u_k(x) \ ,$$

with the definition

$$u_k(x) \equiv \sum_G C(k-G)\, e^{-iGx} \ .$$

Because $u_k(x)$ is a Fourier series over the reciprocal lattice vectors, it is invariant under a crystal lattice translation T, so that $u_k(x) = u_k(x+T)$. We verify this directly by evaluating $u_k(x+T)$:

$$u_k(x+T) = \sum C(k-G) e^{-iG(x+T)} = e^{-iGT} [\sum C(k-G)\, e^{-iGx}] = e^{-iGT} u_k(x) \ .$$

Because $\exp(-iGT) = 1$ by (2.17), it follows that $u_k(x+T) = u_k(x)$, thereby establishing the periodicity of u_k. This is an alternate and exact proof of the Bloch theorem and is valid even when the ψ_k are degenerate.

Crystal Momentum of an Electron

What is the significance of the wavevector $\mathbf{k}$ used to label the Bloch function? It has several properties:

- Under a crystal lattice translation which carries $\mathbf{r}$ to $\mathbf{r} + \mathbf{T}$ we have

$$\psi_{\mathbf{k}}(\mathbf{r}+\mathbf{T}) = e^{i\mathbf{k}\cdot\mathbf{T}} e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}+\mathbf{T}) = e^{i\mathbf{k}\cdot\mathbf{T}}\, \psi_{\mathbf{k}}(\mathbf{r}) \ , \tag{30}$$

  because $u_{\mathbf{k}}(\mathbf{r}+\mathbf{T}) = u_{\mathbf{k}}(\mathbf{r})$. Thus $\exp(i\mathbf{k}\cdot\mathbf{T})$ is the phase factor by which a Bloch function is multiplied when we make a crystal lattice translation $\mathbf{T}$.
- If the lattice potential vanishes, the central equation (27) reduces to $(\lambda_{\mathbf{k}} - \epsilon)C(\mathbf{k}) = 0$, so that all $C(\mathbf{k}-\mathbf{G})$ are zero except $C(\mathbf{k})$, and thus $u_{\mathbf{k}}(\mathbf{r})$ is constant. We have $\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}$, just as for a free electron. (This assumes we have had the foresight to pick the "right" $\mathbf{k}$ as the label. For many purposes other choices of $\mathbf{k}$, differing by a reciprocal lattice vector, will be more convenient.)
- The quantity $\mathbf{k}$ enters in the conservation laws that govern collision processes in crystals. (The conservation laws are really selection rules for transitions.) Thus $\hbar\mathbf{k}$ is called the **crystal momentum** of an electron. If an electron $\mathbf{k}$ absorbs in a collision a phonon of wavevector $\mathbf{q}$, the selection rule is $\mathbf{k} + \mathbf{q} = \mathbf{k}' + \mathbf{G}$. In this process the electron is scattered from a state $\mathbf{k}$ to a state $\mathbf{k}'$, with $\mathbf{G}$ a reciprocal lattice vector. Any arbitrariness in labeling the Bloch functions can be absorbed in the $\mathbf{G}$ without changing the physics of the process.

Solution of the Central Equation

The central equation (27),

$$(\lambda_k - \epsilon)C(k) + \sum_G U_G C(k - G) = 0 \ , \tag{31}$$

represents a set of simultaneous linear equations that connect the coefficients $C(k - G)$ for all reciprocal lattice vectors G. It is a set because there are as many equations as there are coefficients C. These equations are consistent if the determinant of the coefficients vanishes.

Let us write out the equations for an explicit problem. We let g denote the shortest G. We suppose that the potential energy $U(x)$ contains only a single Fourier component $U_g = U_{-g}$, denoted by U. Then a block of the determinant of the coefficients is given by:

$$\begin{array}{ccccc} \lambda_{k-2g} - \epsilon & U & 0 & 0 & 0 \\ U & \lambda_{k-g} - \epsilon & U & 0 & 0 \\ 0 & U & \lambda_k - \epsilon & U & 0 \\ 0 & 0 & U & \lambda_{k+g} - \epsilon & U \\ 0 & 0 & 0 & U & \lambda_{k+2g} - \epsilon \end{array} \ . \tag{32}$$

To see this, write out five successive equations of the set (31). The determinant in principle is infinite in extent, but it will often be sufficient to set equal to zero the portion we have shown.

At a given k, each root ϵ or ϵ_k lies on a different energy band, except in case of coincidence. The solution of the determinant (32) gives a set of energy eigenvalues ϵ_{nk}, where n is an index for ordering the energies and k is the wavevector that labels C_k.

Most often k will be taken in the first zone, to reduce possible confusion in the labeling. If we chose a k different from the original by some reciprocal lattice vector, we would have obtained the same set of equations in a different order—but having the same energy spectrum.

Kronig-Penney Model in Reciprocal Space

As an example of the use of the central equation (31) for a problem that is exactly solvable, we use the Kronig-Penney model of a periodic delta-function potential:

$$U(x) = 2\sum_{G>0} U_G \cos Gx = Aa\sum_s \delta(x - sa) \ , \tag{33}$$

where A is a constant and a the lattice spacing. The sum is over all integers s between 0 and $1/a$. The boundary conditions are periodic over a ring of unit length, which means over $1/a$ atoms. Thus the Fourier coefficients of the potential are

$$\begin{aligned} U_G &= \int_0^1 dx\, U(x) \cos Gx = Aa\sum_s \int_0^1 dx\, \delta(x - sa) \cos Gx \\ &= Aa \sum_s \cos Gsa = A \ . \end{aligned} \tag{34}$$

All U_G are equal for the delta-function potential.

We write the central equation with k as the Bloch index. Thus (31) becomes

$$(\lambda_k - \epsilon)C(k) + A\sum_n C(k - 2\pi n/a) = 0 \ , \tag{35}$$

where $\lambda_k \equiv \hbar^2 k^2/2m$ and the sum is over all integers n. We want to solve (35) for $\epsilon(k)$.

We define

$$f(k) = \sum_n C(k - 2\pi n/a) \ , \tag{36}$$

so that (35) becomes

$$C(k) = -\frac{(2mA/\hbar^2) f(k)}{k^2 - (2m\epsilon/\hbar^2)} \ . \tag{37}$$

Because the sum (36) is over all coefficients C, we have, for any n,

$$f(k) = f(k - 2\pi n/a) \ . \tag{38}$$

This relation lets us write

$$C(k - 2\pi n/a) = -(2mA/\hbar^2) f(k)[(k - 2\pi n/a)^2 - 2m\epsilon/\hbar^2)]^{-1} \ . \tag{39}$$

We sum both sides over all n to obtain, using (36) and cancelling $f(k)$ from both sides,

$$(\hbar^2/2mA) = -\sum_n [(k - 2\pi n/a)^2 - (2m\epsilon/\hbar^2)]^{-1} \ . \tag{40}$$

The sum can be carried out with the help of the standard relation

$$\text{cot} \quad \operatorname{ctn} x = \sum_n \frac{1}{n\pi + x} \ . \tag{41}$$

After trigonometric manipulations in which we use relations for the difference of two cotangents and the product of two sines, the sum in (40) becomes

$$\frac{a^2 \sin Ka}{4Ka(\cos ka - \cos Ka)} \ , \tag{42}$$

where we write $K^2 = 2m\epsilon/\hbar^2$ as in (13).

The final result for (40) is

$$(mAa^2/2\hbar^2)(Ka)^{-1}\sin Ka + \cos Ka = \cos ka \ , \tag{43}$$

which agrees with the Kronig-Penney result (21b) with P written for $mAa^2/2\hbar^2$.

Empty Lattice Approximation

Actual band structures are usually exhibited as plots of energy versus wavevector in the first Brillouin zone. When wavevectors happen to be given outside the first zone, they are carried back into the first zone by subtracting a suitable reciprocal lattice vector. Such a translation can always be found. The operation is helpful in visualization.

When band energies are approximated fairly well by free electron energies $\epsilon_{\mathbf{k}} = \hbar^2\mathbf{k}^2/2m$, it is advisable to start a calculation by carrying the free electron energies back into the first zone. The procedure is simple enough once one gets the hang of it. We look for a $\mathbf{G}$ such that a $\mathbf{k}'$ in the first zone satisfies

$$\mathbf{k}' + \mathbf{G} = \mathbf{k} \ ,$$

where $\mathbf{k}$ is unrestricted and is the true free electron wavevector in the empty lattice. (Once the plane wave is modulated by the lattice, there is no single "true" wavevector for the state ψ.)

If we drop the prime on $\mathbf{k}'$ as unnecessary baggage, the free electron energy can always be written as

$$\begin{aligned}\epsilon(k_x,k_y,k_z) &= (\hbar^2/2m)(\mathbf{k} + \mathbf{G})^2 \\ &= (\hbar^2/2m)[(k_x + G_x)^2 + (k_y + G_y)^2 + (k_z + G_z)^2] \ ,\end{aligned}$$

with $\mathbf{k}$ in the first zone and $\mathbf{G}$ allowed to run over the appropriate reciprocal lattice points.

We consider as an example the low-lying free electron bands of a simple cubic lattice. Suppose we want to exhibit the energy as a function of $\mathbf{k}$ in the [100] direction. For convenience, choose units such that $\hbar^2/2m = 1$. We show several low-lying bands in this empty lattice approximation with their energies $\epsilon(000)$ at $\mathbf{k} = 0$ and $\epsilon(k_x00)$ along the k_x axis in the first zone:

Band	$Ga/2\pi$	$\epsilon(000)$	$\epsilon(k_x00)$
1	000	0	k_x^2
2,3	$100,\bar{1}00$	$(2\pi/a)^2$	$(k_x \pm 2\pi/a)^2$
4,5,6,7	$010,0\bar{1}0,001,00\bar{1}$	$(2\pi/a)^2$	$k_x^2 + (2\pi/a)^2$
8,9,10,11	$110,101,1\bar{1}0,10\bar{1}$	$2(2\pi/a)^2$	$(k_x + 2\pi/a)^2 + (2\pi/a)^2$
12,13,14,15	$\bar{1}10,\bar{1}01,\bar{1}\bar{1}0,\bar{1}0\bar{1}$	$2(2\pi/a)^2$	$(k_x - 2\pi/a)^2 + (2\pi/a)^2$
16,17,18,19	$011,0\bar{1}1,01\bar{1},0\bar{1}\bar{1}$	$2(2\pi/a)^2$	$k_x^2 + 2(2\pi/a)^2$

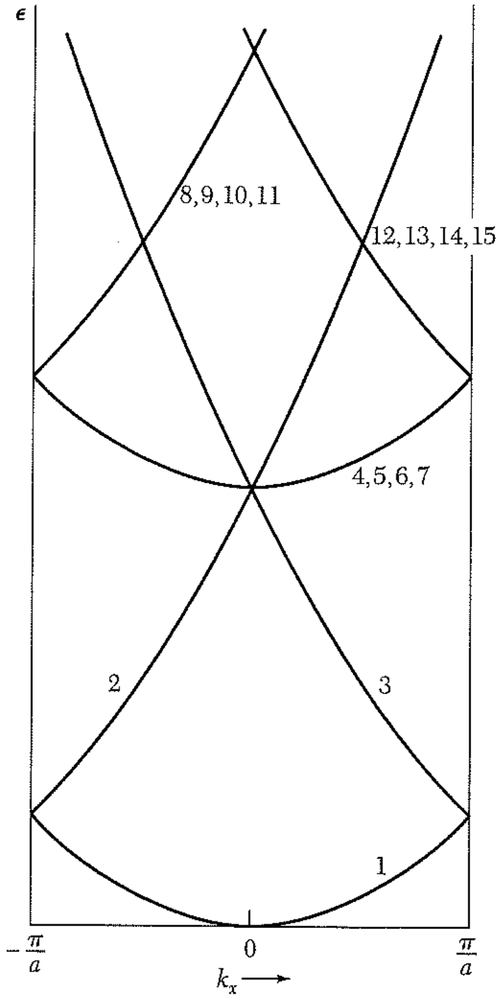


Figure 8 Low-lying free electron energy bands of the empty *sc* lattice, as transformed to the first Brillouin zone and plotted vs. (k_x00). The free electron energy is $\hbar^2(\mathbf{k}+\mathbf{G})^2/2m$, where the **G**'s are given in the second column of the table. The bold curves are in the first Brillouin zone, with $-\pi/a \le k_x \le \pi/a$. Energy bands drawn in this way are said to be in the reduced zone scheme.

These free electron bands are plotted in Fig. 8. It is a good exercise to plot the same bands for **k** parallel to the [111] direction of wavevector space.

Approximate Solution Near a Zone Boundary

We suppose that the Fourier components U_G of the potential energy are small in comparison with the kinetic energy of a free electron at the zone boundary. We first consider a wavevector exactly at the zone boundary at $\frac{1}{2}G$, that is, at π/a. Here

$$k^2 = (\tfrac{1}{2}G)^2 \ ; \quad (k-G)^2 = (\tfrac{1}{2}G - G)^2 = (\tfrac{1}{2}G)^2 \ ,$$

so that at the zone boundary the kinetic energy of the two component waves $k = \pm\frac{1}{2}G$ are equal.

If $C(\frac{1}{2}G)$ is an important coefficient in the orbital (29) at the zone boundary, then $C(-\frac{1}{2}G)$ is also an important coefficient. This result also follows from the discussion of (5). We retain only those equations in the central equation that contain both coefficients $C(\frac{1}{2}G)$ and $C(-\frac{1}{2}G)$, and neglect all other coefficients.

One equation of (31) becomes, with $k = \frac{1}{2}G$ and $\lambda = \hbar^2(\frac{1}{2}G)^2/2m$,

$$(\lambda - \epsilon)C(\tfrac{1}{2}G) + UC(-\tfrac{1}{2}G) = 0 \ . \tag{44}$$

Another equation of (31) becomes, with $k = \frac{1}{2}G$,

$$(\lambda - \epsilon)C(-\tfrac{1}{2}G) + UC(\tfrac{1}{2}G) = 0 \ . \tag{45}$$

These two equations have nontrivial solutions for the two coefficients if the energy ϵ satisfies

$$\begin{vmatrix} \lambda - \epsilon & U \\ U & \lambda - \epsilon \end{vmatrix} = 0 \ , \tag{46}$$

whence

$$(\lambda - \epsilon)^2 = U^2 \ ; \qquad \epsilon = \lambda \pm U = \frac{\hbar^2}{2m}(\tfrac{1}{2}G)^2 \pm U \ . \tag{47}$$

The energy has two roots, one lower than the free electron kinetic energy by U, and one higher by U. Thus the potential energy $2U \cos Gx$ has created an energy gap $2U$ at the zone boundary.

The ratio of the C's may be found from either (44) or (45):

$$\frac{C(-\frac{1}{2}G)}{C(\frac{1}{2}G)} = \frac{\epsilon - \lambda}{U} = \pm 1 \ , \tag{48}$$

where the last step uses (47). Thus the Fourier expansion of $\psi(x)$ at the zone boundary has the two solutions

$$\psi(x) = \exp(iGx/2) \pm \exp(-iGx/2) \ .$$

These orbitals are identical to (5).

One solution gives the wavefunction at the bottom of the energy gap; the other gives the wavefunction at the top of the gap. Which solution has the lower energy depends on the sign of U.

We now solve for orbitals with wavevector k near the zone boundary $\frac{1}{2}G$. We use the same two-component approximation, now with a wavefunction of the form

$$\psi(x) = C(k)\, e^{ikx} + C(k - G)\, e^{i(k-G)x} \ . \tag{49}$$

As directed by the central equation (31), we solve the pair of equations

$$(\lambda_k - \epsilon)C(k) + UC(k - G) = 0 \ ;$$

$$(\lambda_{k-G} - \epsilon)C(k - G) + UC(k) = 0 \ ,$$

with λ_k defined as $\hbar^2k^2/2m$. These equations have a solution if the energy ϵ satisfies

$$\begin{vmatrix} \lambda_k - \epsilon & U \\ U & \lambda_{k-G} - \epsilon \end{vmatrix} = 0 \ ,$$

whence $\epsilon^2 - \epsilon(\lambda_{k-G} + \lambda_k) + \lambda_{k-G}\lambda_k - U^2 = 0$.

The energy has two roots:

$$\epsilon = \tfrac{1}{2}(\lambda_{k-G} + \lambda_k) \pm [\tfrac{1}{4}(\lambda_{k-G} - \lambda_k)^2 + U^2]^{1/2} \ , \tag{50}$$

and each root describes an energy band, plotted in Fig. 9. It is convenient to expand the energy in terms of a quantity $\tilde{K}$ (the mark over the K is called a tilde), which measures the difference $\tilde{K} \equiv k - \frac{1}{2}G$ in wavevector between k and the zone boundary:

$$\begin{aligned} \epsilon_{\tilde{K}} &= (\hbar^2/2m)(\tfrac{1}{4}G^2 + \tilde{K}^2) \pm [4\lambda(\hbar^2\tilde{K}^2/2m) + U^2]^{1/2} \\ &\simeq (\hbar^2/2m)(\tfrac{1}{4}G^2 + \tilde{K}^2) \pm U[1 + 2(\lambda/U^2)(\hbar^2\tilde{K}^2/2m)] \ , \end{aligned} \tag{51}$$

in the region $\hbar^2G\tilde{K}/2m \ll |U|$. Here $\lambda = (\hbar^2/2m)(\frac{1}{2}G)^2$ as before.

Writing the two zone boundary roots of (47) as $\epsilon(\pm)$, we may write (51) as

$$\epsilon_{\tilde{K}}(\pm) = \epsilon(\pm) + \frac{\hbar^2\tilde{K}^2}{2m}\left(1 \pm \frac{2\lambda}{U}\right) \ . \tag{52}$$

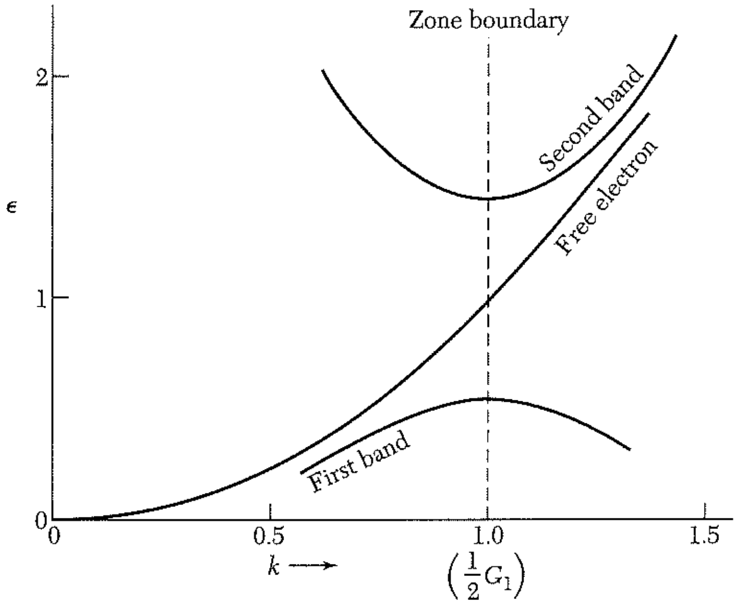


Figure 9 Solutions of (50) in the periodic zone scheme, in the region near a boundary of the first Brillouin zone. The units are such that $U = -0.45$, $G = 2$, and $\hbar^2/m = 1$. The free electron curve is drawn for comparison. The energy gap at the zone boundary is 0.90. The value of U has deliberately been chosen large for this illustration, too large for the two-term approximation to be accurate.

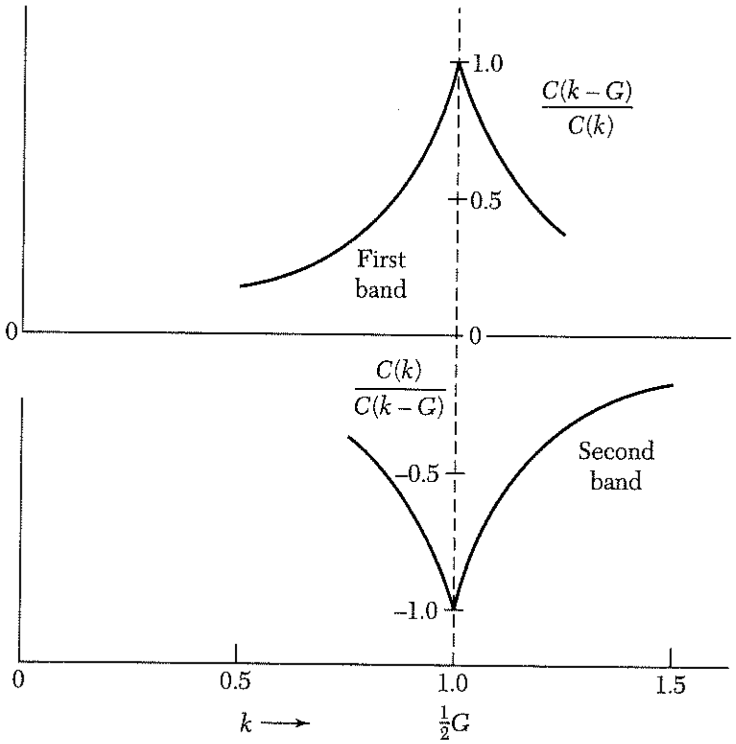


Figure 10 Ratio of the coefficients in $\psi(x) = C(k)\exp(ikx) + C(k - G)\exp[i(k - G)x]$ as calculated near the boundary of the first Brillouin zone. One component dominates as we move away from the boundary.

These are the roots for the energy when the wavevector is very close to the zone boundary at $\frac{1}{2}G$. Note the quadratic dependence of the energy on the wavevector $\tilde{K}$. For U negative, the solution $\epsilon(-)$ corresponds to the upper of the two bands, and $\epsilon(+)$ to the lower of the two bands. The two C's are plotted in Fig. 10.

NUMBER OF ORBITALS IN A BAND

Consider a linear crystal constructed of an even number N of primitive cells of lattice constant a. In order to count states we apply periodic boundary conditions to the wavefunctions over the length of the crystal. The allowed values of the electron wavevector k in the first Brillouin zone are given by (2):

$$k = 0\ ; \quad \pm\frac{2\pi}{L}\ ; \quad \pm\frac{4\pi}{L}\ ; \ \ldots\ ; \ \frac{N\pi}{L}\ . \tag{53}$$

We cut the series off at $N\pi/L = \pi/a$, for this is the zone boundary. The point $-N\pi/L = -\pi/a$ is not to be counted as an independent point because it is connected by a reciprocal lattice vector with π/a. The total number of points is exactly N, the number of primitive cells.

Each primitive cell contributes exactly one independent value of k to each energy band. This result carries over into three dimensions. With account taken of the two independent orientations of the electron spin, **there**

are **$2N$ independent orbitals in each energy band**. If there is a single atom of valence, one in each primitive cell, the band can be half filled with electrons. If each atom contributes two valence electrons to the band, the band can be exactly filled. If there are two atoms of valence, one in each primitive cell, the band can also be exactly filled.

Metals and Insulators

If the valence electrons exactly fill one or more bands, leaving others empty, the crystal will be an insulator. An external electric field will not cause current flow in an insulator. (We suppose that the electric field is not strong enough to disrupt the electronic structure.) Provided that a filled band is separated by an energy gap from the next higher band, there is no continuous way to change the total momentum of the electrons if every accessible state is filled. Nothing changes when the field is applied. This is quite unlike the situation for free electrons for which $\mathbf{k}$ increases uniformly in a field (Chapter 6).

A crystal can be an insulator only if the number of valence electrons in a primitive cell of the crystal is an even integer. (An exception must be made for electrons in tightly bound inner shells which cannot be treated by band theory.) If a crystal has an even number of valence electrons per primitive cell, it is necessary to consider whether or not the bands overlap in energy. If the bands overlap in energy, then instead of one filled band giving an insulator, we can have two partly filled bands giving a metal (Fig. 11).

The alkali metals and the noble metals have one valence electron per primitive cell, so that they have to be metals. The alkaline earth metals have two valence electrons per primitive cell; they could be insulators, but the bands overlap in energy to give metals, but not very good metals. Diamond, silicon, and germanium each have two atoms of valence four, so that there are

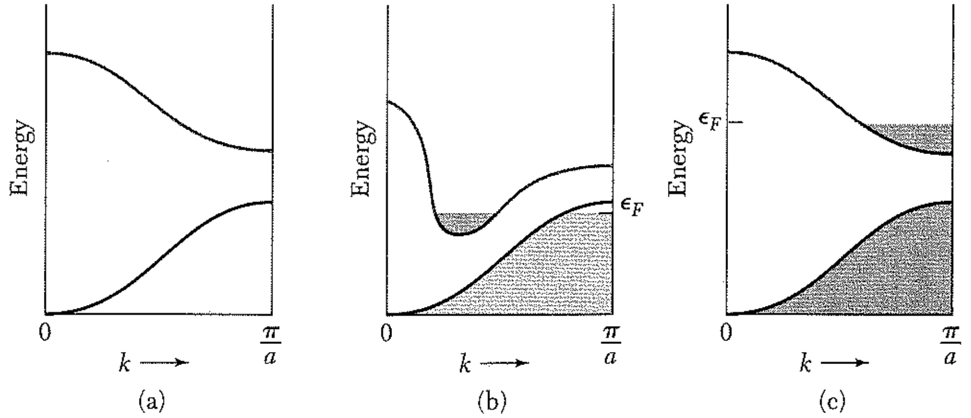


Figure 11 Occupied states and band structures giving (a) an insulator, (b) a metal or a semimetal because of band overlap, and (c) a metal because of electron concentration. In (b) the overlap need not occur along the same directions in the Brillouin zone. If the overlap is small, with relatively few states involved, we speak of a semimetal.

eight valence electrons per primitive cell; the bands do not overlap, and the pure crystals are insulators at absolute zero.

SUMMARY

- The solutions of the wave equation in a periodic lattice are of the Bloch form $\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}\, u_{\mathbf{k}}(\mathbf{r})$, where $u_{\mathbf{k}}(\mathbf{r})$ is invariant under a crystal lattice translation.
- There are regions of energy for which no Bloch function solutions of the wave equation exist (see Problem 5). These energies form forbidden regions in which the wavefunctions are damped in space and the values of the **k**'s are complex, as pictured in Fig. 12. The existence of forbidden regions of energy is prerequisite to the existence of insulators.
- Energy bands may often be approximated by one or two plane waves: for example, $\psi_k(x) \cong C(k)e^{ikx} + C(k - G)e^{i(k-G)x}$ near the zone boundary at $\frac{1}{2}G$.
- The number of orbitals in a band is $2N$, where N is the number of primitive cells in the specimen.

Problems

1. ***Square lattice, free electron energies.*** (a) Show for a simple square lattice (two dimensions) that the kinetic energy of a free electron at a corner of the first zone is higher than that of an electron at midpoint of a side face of the zone by a factor of 2. (b) What is the corresponding factor for a simple cubic lattice (three dimensions)? (c) What bearing might the result of (b) have on the conductivity of divalent metals?
2. ***Free electron energies in reduced zone.*** Consider the free electron energy bands of an fcc crystal lattice in the approximation of an empty lattice, but in the reduced zone scheme in which all **k**' s are transformed to lie in the first Brillouin zone. Plot roughly in the [111] direction the energies of all bands up to six times the lowest band energy at the zone boundary at $\mathbf{k} = (2\pi/a)(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Let this be the unit of energy. This problem shows why band edges need not necessarily be at the zone center. Several of the degeneracies (band crossings) will be removed when account is taken of the crystal potential.
3. ***Kronig-Penney model.*** (a) For the delta-function potential and with $P \ll 1$, find at $k = 0$ the energy of the lowest energy band. (b) For the same problem find the band gap at $k = \pi/a$.
4. ***Potential energy in the diamond structure.*** (a) Show that for the diamond structure the Fourier component U_G of the crystal potential seen by an electron is equal to zero for $\mathbf{G} = 2\mathbf{A}$, where **A** is a basis vector in the reciprocal lattice referred to the conventional cubic cell. (b) Show that in the usual first-order approximation to the solutions of the wave equation in a periodic lattice the energy gap vanishes at the zone boundary plane normal to the end of the vector **A**.

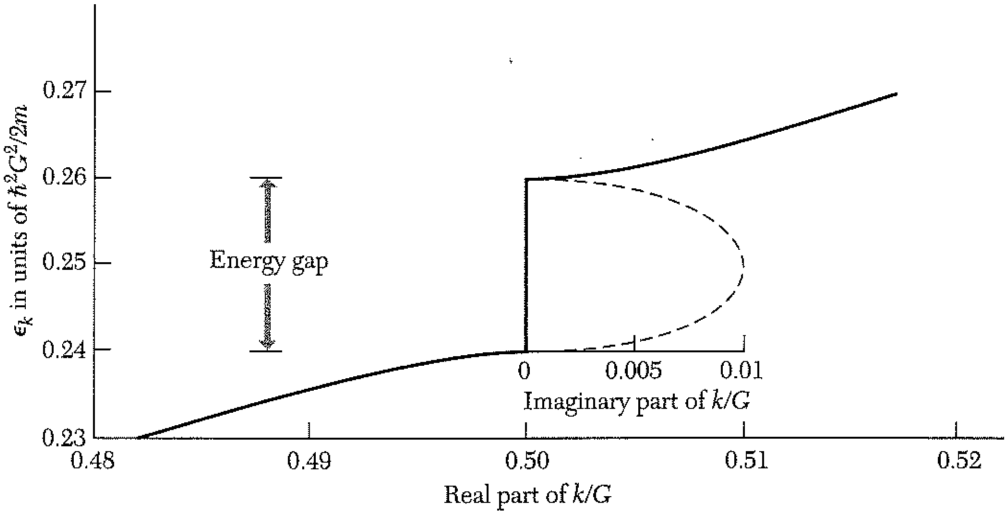


Figure 12 In the energy gap there exist solutions of the wave equation for complex values of the wavevector. At the boundary of the first zone the real part of the wavevector is $\frac{1}{2}G$. The imaginary part of k in the gap is plotted in the approximation of two plane waves, for $U = 0.01\ \hbar^2G^2/2m$. In an infinite unbounded crystal the wavevector must be real, or else the amplitude will increase without limit. But on a surface or at a junction there can exist solutions with complex wavevector.

*5. ***Complex wavevectors in the energy gap.*** Find an expression for the imaginary part of the wavevector in the energy gap at the boundary of the first Brillouin zone, in the approximation that led to Eq. (46). Give the result for the Im(k) at the center of the energy gap. The result for small Im(k) is

$$(\hbar^2/2m)[\mathrm{Im}(k)]^2 \approx 2mU^2/\hbar^2G^2 \ .$$

The form as plotted in Fig. 12 is of importance in the theory of Zener tunneling from one band to another in the presence of a strong electric field.

6. ***Square lattice.*** Consider a square lattice in two dimensions with the crystal potential

$$U(x,y) = -4U\cos(2\pi x/a)\cos(2\pi y/a) \ .$$

Apply the central equation to find approximately the energy gap at the corner point $(\pi/a,\ \pi/a)$ of the Brillouin zone. It will suffice to solve a 2 × 2 determinantal equation.

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*This problem is somewhat difficult.