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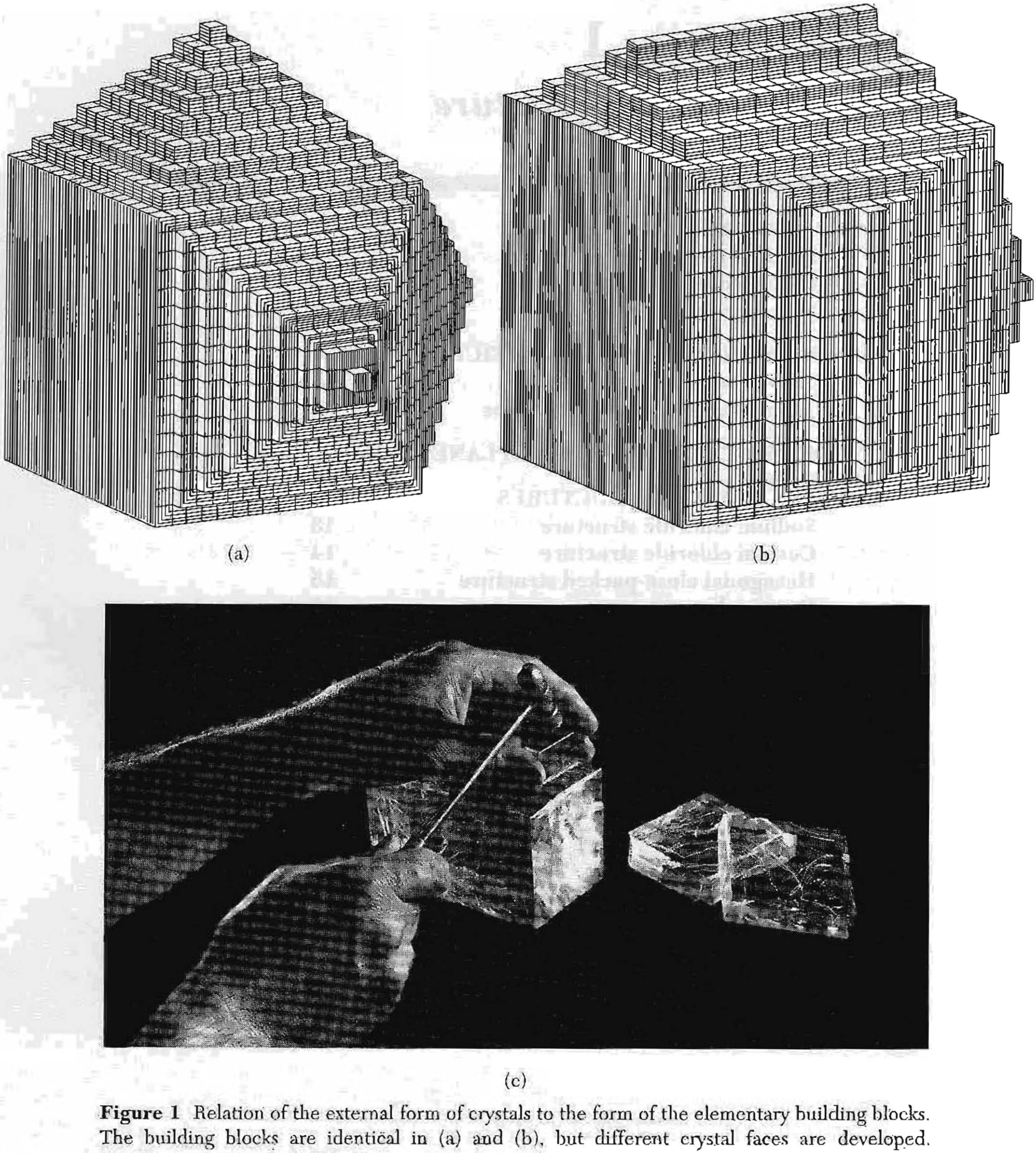
Crystal Structure

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.

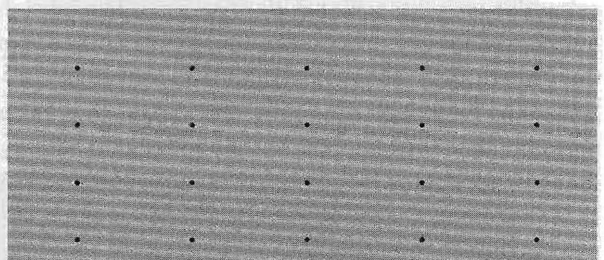
Lattice Translation Vectors

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:

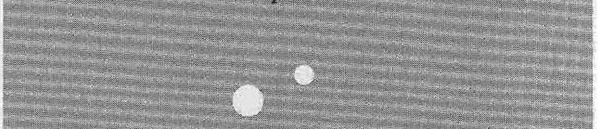
$$\mathbf{r}' = \mathbf{r} + u_1\mathbf{a}_1 + u_2\mathbf{a}_2 + u_3\mathbf{a}_3 . \tag{1}$$

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.

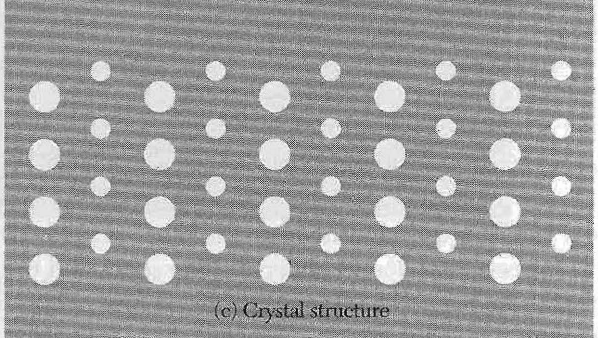
The lattice is said to be **primitive** if any two points from which the atomic arrangement looks the same always satisfy (1) with a suitable choice of the integers u_i. This statement defines the **primitive translation vectors** $\mathbf{a}_i$. There is no cell of smaller volume than $\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3$ 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.



(a) Space lattice



(b) Basis, containing two different ions



(c) Crystal 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.

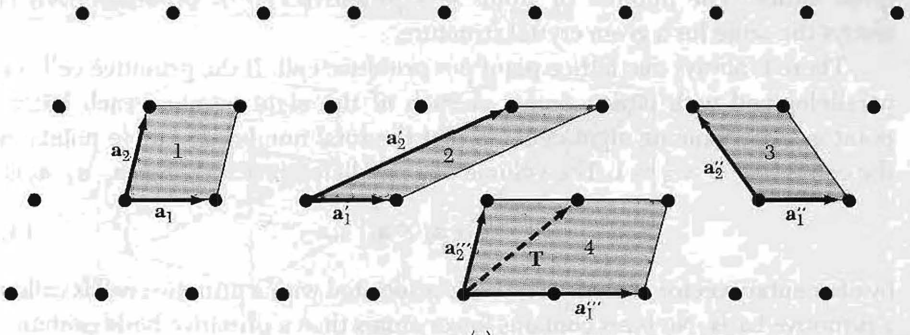
Basis and the Crystal Structure

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.

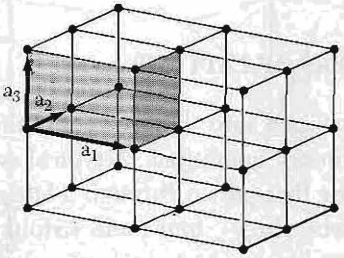
The number of atoms in the basis may be one, or it may be more than one. The position of the center of an atom j of the basis relative to the associated lattice point is

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

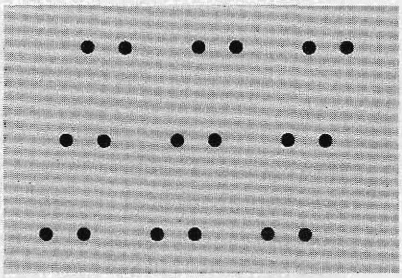
We may arrange the origin, which we have called the associated lattice point, so that $0 \le x_j, y_j, z_j \le 1$.



(a)



(b)



(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.

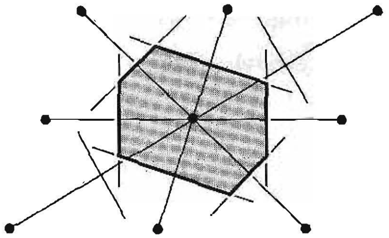


Figure 4 A primitive cell may also be chosen following this procedure: (1) draw lines to connect a given lattice point to all nearby lattice points; (2) at the midpoint and normal to these lines, draw new lines or planes. The smallest volume enclosed in this way is the Wigner-Seitz primitive cell. All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

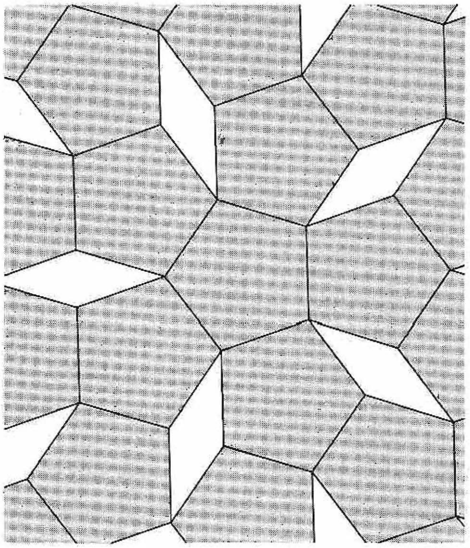


Figure 5 A fivefold axis of symmetry cannot exist in a periodic lattice because it is not possible to fill the area of a plane with a connected array of pentagons. We can, however, fill all the area of a plane with just two distinct designs of "tiles" or elementary polygons.

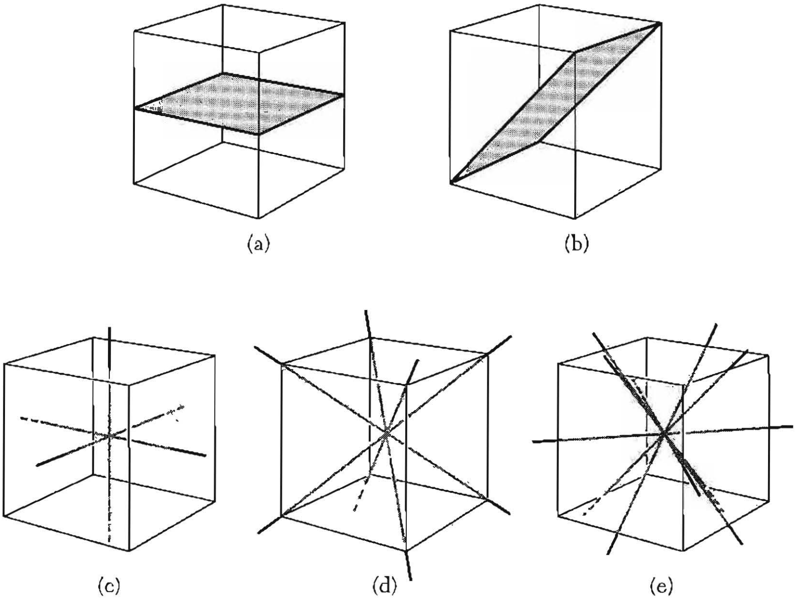


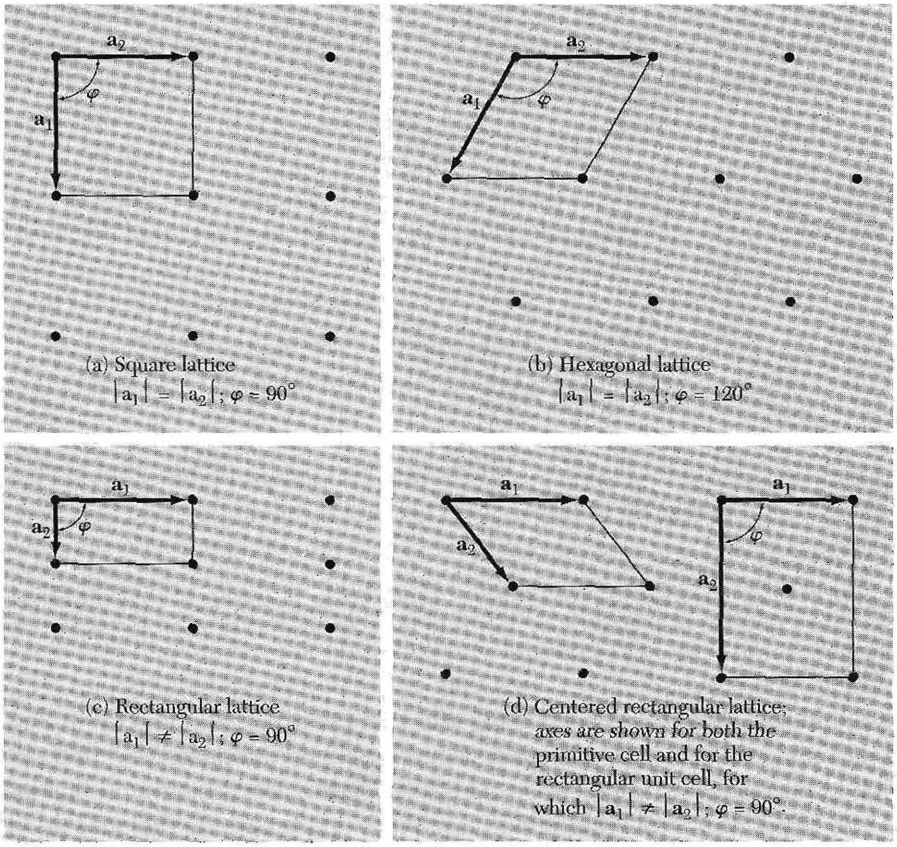
Figure 6 (a) A plane of symmetry parallel to the faces of a cube. (b) A diagonal plane of symmetry in a cube. (c) The three tetrad axes of a cube. (d) The four triad axes of a cube. (e) The six diad axes of a cube.

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	$a_1 = a_2 \neq a_3$ $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$

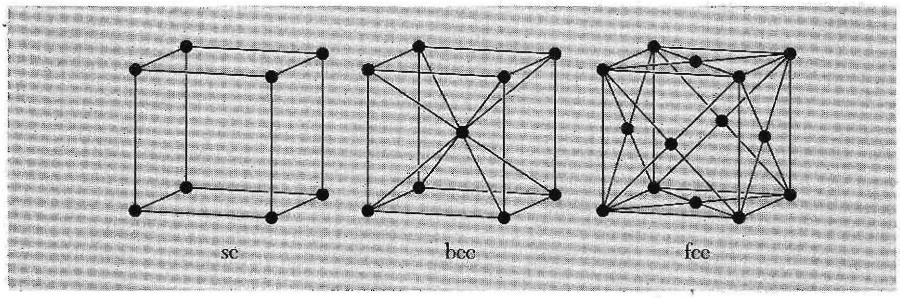


Figure 8 The cubic space lattices. The cells shown are the conventional cells.

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.

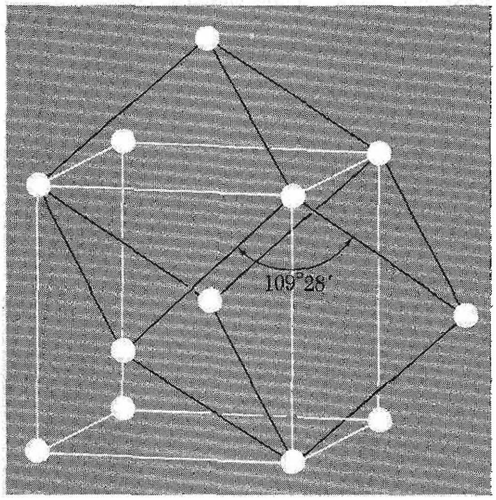


Figure 9 Body-centered cubic lattice, showing a primitive cell. The primitive cell shown is a rhombohedron of edge $\frac{1}{2}\sqrt{3}\,a$, and the angle between adjacent edges is 109°28′.

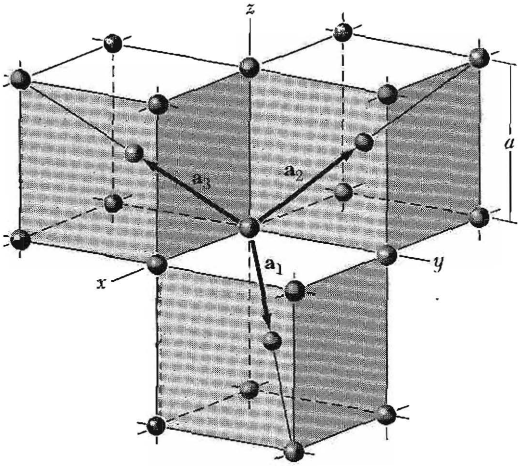


Figure 10 Primitive translation vectors of the body-centered cubic lattice; these vectors connect the lattice point at the origin to lattice points at the body centers. The primitive cell is obtained on completing the rhombohedron. In terms of the cube edge a, the primitive translation vectors are

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

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

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.

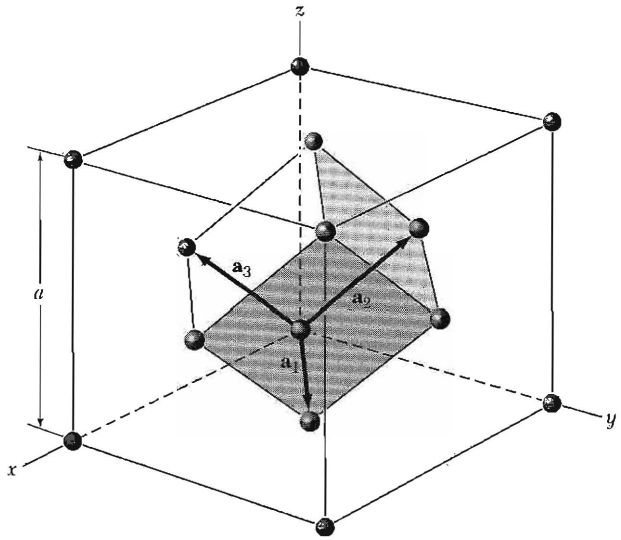


Figure 11 The rhombohedral primitive cell of the face-centered cubic crystal. The primitive translation vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ connect the lattice point at the origin with lattice points at the face centers. As drawn, the primitive vectors are:

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

The angles between the axes are 60°.

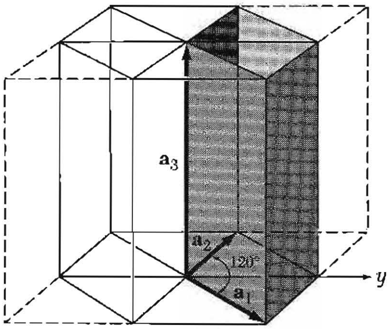


Figure 12 Relation of the primitive cell in the hexagonal system (heavy lines) to a prism of hexagonal symmetry. Here $a_1 = a_2 \neq a_3$.

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.

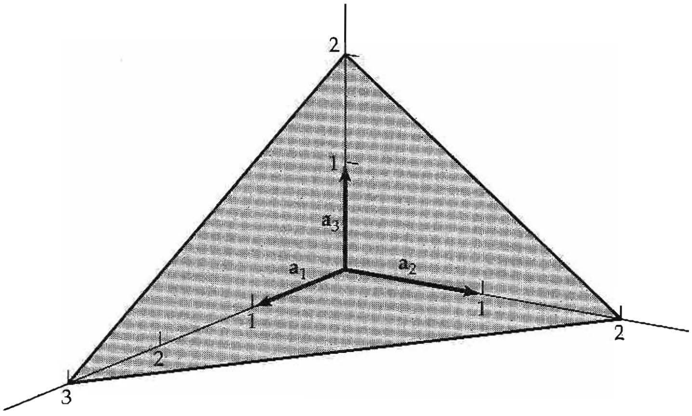
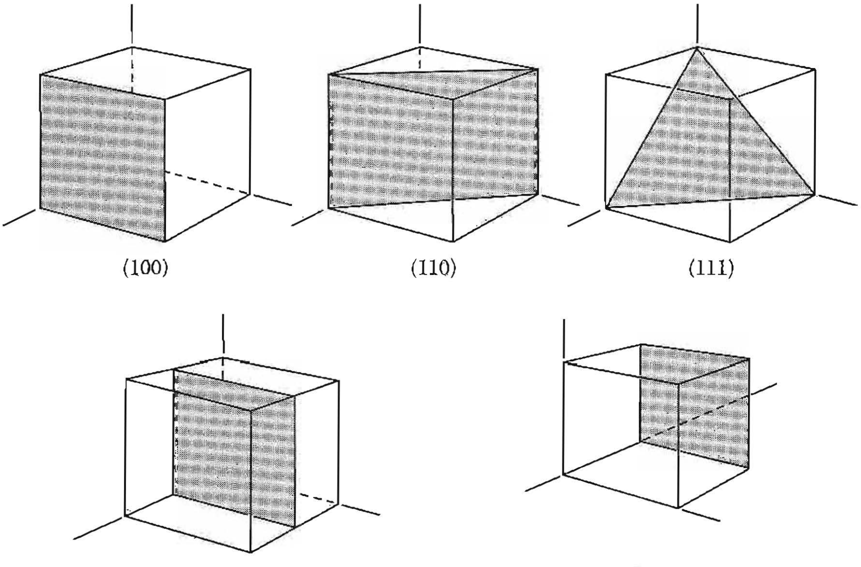


Figure 13 This plane intercepts the $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ axes at $3\mathbf{a}_1$, $2\mathbf{a}_2$, $2\mathbf{a}_3$. The reciprocals of these numbers are $\frac{1}{3}$, $\frac{1}{2}$, $\frac{1}{2}$. The smallest three integers having the same ratio are 2, 3, 3, and thus the indices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

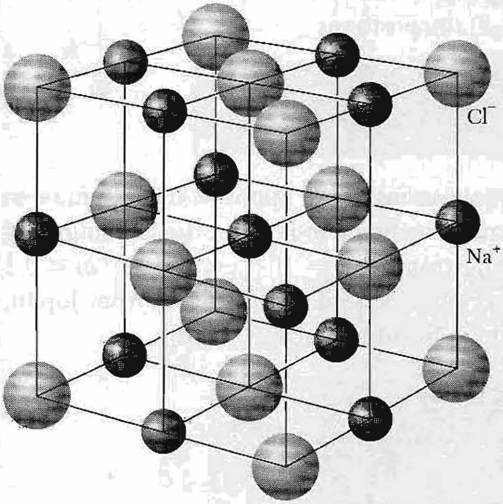


Figure 15 We may construct the sodium chloride crystal structure by arranging Na^+ and Cl^- ions alternately at the lattice points of a simple cubic lattice. In the crystal each ion is surrounded by six nearest neighbors of the opposite charge. The space lattice is fcc, and the basis has one Cl^- ion 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.

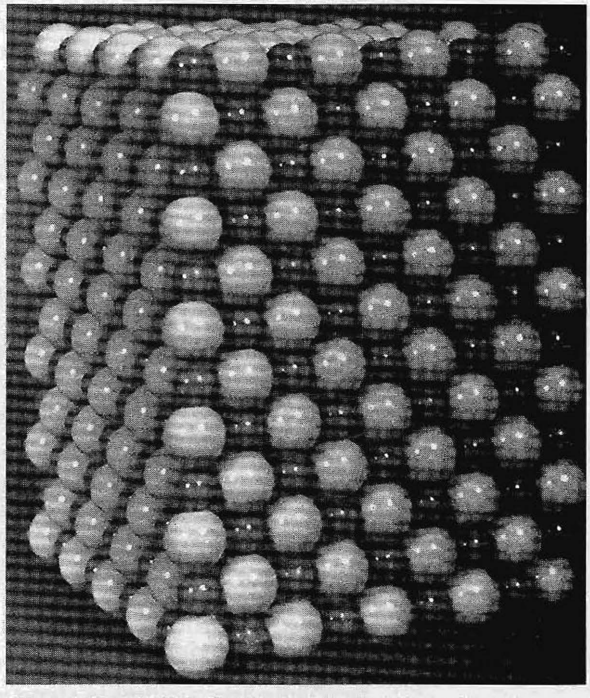


Figure 16 Model of sodium chloride. The sodium ions are smaller than the chlorine ions. (Courtesy of A. N. Holden and P. Singer.)

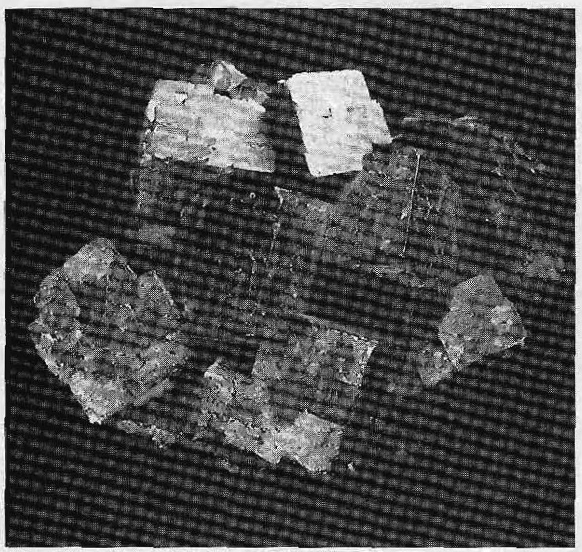


Figure 17 Natural crystals of lead sulfide, PbS, which has the NaCl crystal structure. (Photograph by B. Burleson.)

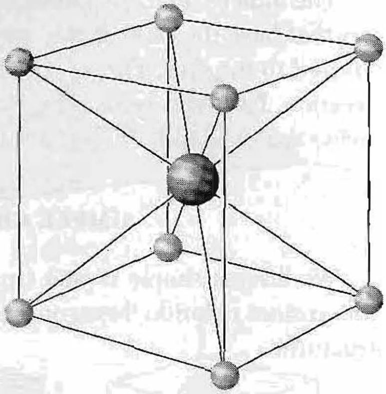


Figure 18 The cesium chloride crystal structure. The space lattice is simple cubic, and the basis has one Cs^+ ion at 000 and one Cl^- ion at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$.

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 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

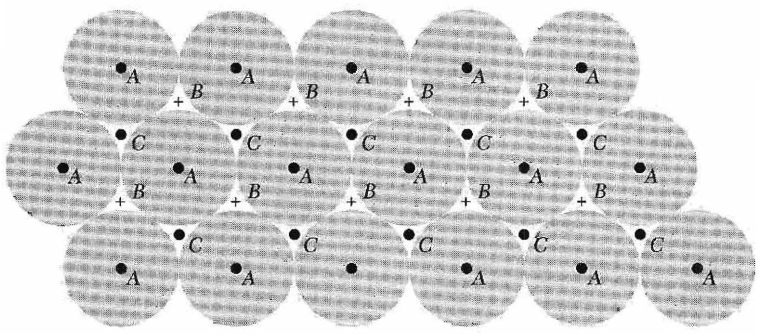


Figure 19 A close-packed layer of spheres is shown, with centers at points marked *A*. A second and identical layer of spheres can be placed on top of this, above and parallel to the plane of the drawing, with centers over the points marked *B*. There are two choices for a third layer. It can go in over *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.

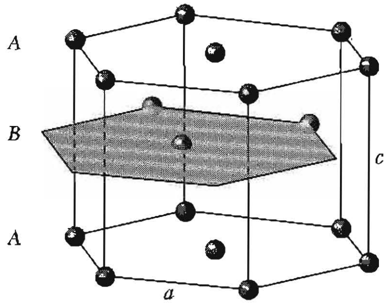


Figure 20 The hexagonal close-packed structure. The atom positions in this structure do not constitute a space lattice. The space lattice is simple hexagonal with a basis of two identical atoms associated with each lattice point. The lattice parameters *a* and *c* are indicated, where *a* is in the basal 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.

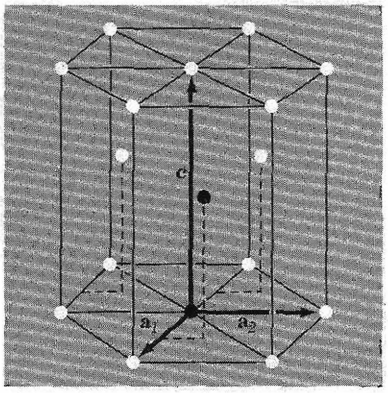


Figure 21 The primitive cell has $a_1 = a_2$, with an included angle of 120°. The c axis (or $\mathbf{a}_3$) is normal to the plane of $\mathbf{a}_1$ and $\mathbf{a}_2$. The ideal hcp structure has $c = 1.633\ a$. The two atoms of one basis are shown as solid circles. One atom of the basis is at the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

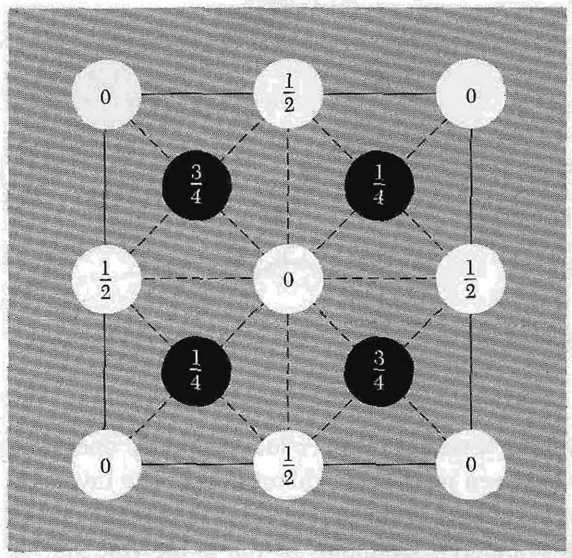


Figure 22 Atomic positions in the cubic cell of the diamond structure projected *on a cube face*; fractions denote height above the base in units of a cube edge. The points at 0 and $\frac{1}{2}$ are on the fcc lattice; those at $\frac{1}{4}$ and $\frac{3}{4}$ are on a similar lattice displaced along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

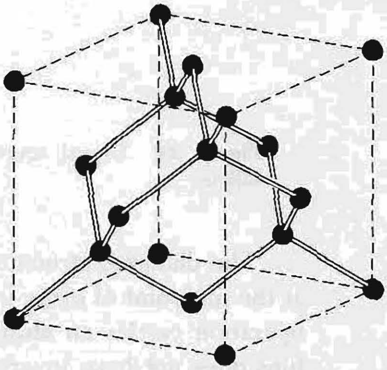


Figure 23 Crystal structure of diamond, showing the tetrahedral bond arrangement.

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.

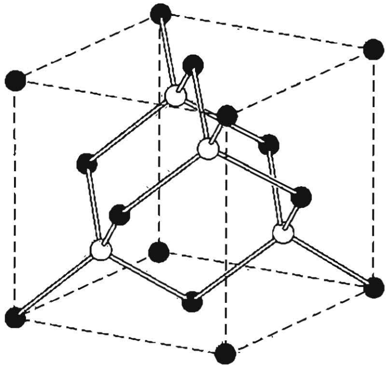


Figure 24 Crystal structure of cubic zinc sulfide.

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 **r** into an atom at −**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

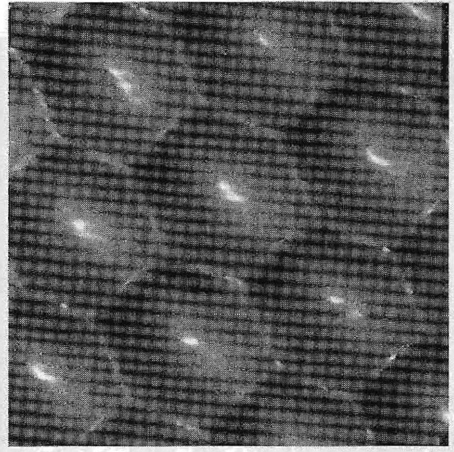


Figure 25 A scanning tunneling microscope image of atoms on a (111) surface of fcc platinum at 4 K. The nearest-neighbor spacing is 2.78 Å. (Photo courtesy of D. M. Eigler, IBM Research Division.)

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

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

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.
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.