3 Crystalline Properties of Solids

3.1 Introduction

This chapter gives a brief introduction to crystallography, which is the science that studies the structure and properties of the crystalline state of matter. We will first discuss the arrangements of atoms in various solids, distinguishing between single crystals and other forms of solids. We will then describe the properties that result from the periodicity in crystal lattices. A few important crystallography terms most often found in solid state devices will be defined and illustrated in crystals having basic structures. These definitions will then allow us to refer to certain planes and directions within a lattice of arbitrary structure.

Investigations of the crystalline state have a long history. Johannes Kepler (*Strena Seu de Nive Sexangula*, 1611) speculated on the question as to why snowflakes always have six corners, never five or seven (Fig. 3.1). It was the first treatise on geometrical crystallography. He showed how the close-packing of spheres gave rise to a six-corner pattern. Next, Robert Hooke (*Micrographia*, 1665) and Rene Just Haüy (*Essai d'une théorie sur la structure des cristaux*, 1784) used close-packing arguments in order to explain the shapes of a number of crystals. These works laid the foundation of the mathematical theory of crystal structure. It is only recently, thanks to x-ray and electron diffraction techniques, that it has been realized that most materials, including biological objects, are crystalline or partly so (Fig. 3.2).

All elements from the periodic table and their compounds, be they gas, liquid, or solid, are composed of atoms, ions, or molecules. Matter is discontinuous. However, since the sizes of the atoms, ions, and molecules lie in the 1 Å (10^{-10} m or 10^{-8} m) region, matter appears continuous to us. The different states of matter may be distinguished by their tendency to retain a characteristic volume and shape. A gas adopts both the volume and shape of its container, a liquid has a constant volume but adopts the shape of its container, while a solid retains both its shape and volume independently of its container. This is illustrated in Fig. 3.3. The natural forms of each element in the periodic table are given in Fig. A1 in Appendix A.3.

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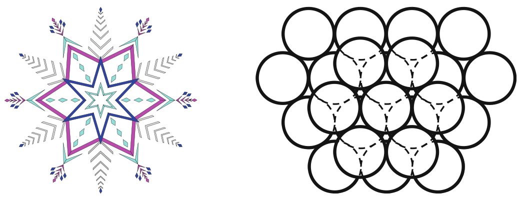


a b

Fig. 3.1 (**a**) Snowflake crystal and (**b**) the close-packing of spheres which gives rise to a six-corner pattern. The close-packing of spheres can be thought as the way to most efficiently stack identical spheres

Gases Molecules or atoms in a gas move rapidly through space and thus have a high kinetic energy. The attractive forces between molecules are comparatively weak and the energy of attraction is negligible in comparison to the kinetic energy.

Liquids As the temperature of a gas is lowered, the kinetic energies of the molecules or atoms decrease. When the boiling point (Fig. A.3 in Appendix A.3) is reached, the kinetic energy will be equal to the energy of attraction among the molecules or atoms. Further cooling thus converts the gas into a liquid. The attractive forces cause the molecules to "touch" one another. They do not, however, maintain fixed positions. The molecules change positions continuously. Small regions of order may indeed be found (local ordering), but if a large enough volume is considered, it will also be seen that liquids give a statistically homogeneous arrangement of molecules and therefore also have isotropic physical properties, i.e., equivalent in all directions. Some special types of liquids that consist of long molecules may reveal anisotropic properties (e.g., liquid crystals).

Solids When the temperature falls below the freezing point, the kinetic energy becomes so small that the molecules become permanently attached to one another. A three-dimensional framework of net attractive interaction forms among the molecules and the array becomes solid. The movement of molecules or atoms in the solid now consists only of vibrations about some fixed positions. A result of these permanent interactions is that the molecules or atoms have become ordered to some extent. The distribution of molecules is no longer statistical but is almost or fully periodically homogeneous, and periodic distribution in three dimensions may be formed.

The distribution of molecules or atoms, when a liquid or a gas cools to the solid state, determines the type of solid. Depending on how the solid is formed, a compound can exist in any of the three forms in Fig. 3.3. The ordered crystalline phase is the stable state with the lowest internal energy (absolute thermal equilibrium). The solid in this state is called the single crystal form. It has an exact periodic arrangement of its building blocks (atoms or molecules).

Sometimes the external conditions at a time of solidification (temperature, pressure, cooling rate) are such that the resulting materials have a periodic arrangement of atoms which is interrupted randomly along two-dimensional sections that can intersect, thus dividing a given volume of a solid into a number of smaller single crystalline regions or grains. The size of these grains can be as small as several p-orbital elements; d-orbital elements; s-orbital elements

Atom symbol — Atomic weight — Atomic number

Principal quantum number	IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIII	VIII	VIII	IB	IIB	IIIB	IVB	VB	VIB	VIIB	VIIIB	Highest atomic shell occupied
n=1	1.008 **H** 1																	4.003 **He** 2	K
n=2	6.941 **Li** 3	9.012 **Be** 4											10.81 **B** 5	12.01 **C** 6	14.01 **N** 7	16.00 **O** 8	19.00 **F** 9	20.18 **Ne** 10	L
n=3	22.99 **Na** 11	24.31 **Mg** 12											26.98 **Al** 13	28.09 **Si** 14	30.97 **P** 15	32.06 **S** 16	35.45 **Cl** 17	39.95 **Ar** 18	M
n=4	39.10 **K** 19	40.08 **Ca** 20	44.96 **Sc** 21	47.88 **Ti** 22	50.94 **V** 23	52.00 **Cr** 24	54.94 **Mn** 25	55.85 **Fe** 26	58.93 **Co** 27	58.70 **Ni** 28	63.55 **Cu** 29	65.38 **Zn** 30	69.72 **Ga** 31	72.59 **Ge** 32	74.92 **As** 33	78.96 **Se** 34	79.90 **Br** 35	83.80 **Kr** 36	N
n=5	85.47 **Rb** 37	87.62 **Sr** 38	88.91 **Y** 39	91.22 **Zr** 40	92.91 **Nb** 41	95.94 **Mo** 42	97.9 **Tc** 43	101.1 **Ru** 44	102.9 **Rh** 45	106.4 **Pd** 46	107.9 **Ag** 47	112.4 **Cd** 48	114.8 **In** 49	118.7 **Sn** 50	121.8 **Sb** 51	127.6 **Te** 52	126.9 **I** 53	131.3 **Xe** 54	O
n=6	132.9 **Cs** 55	137.3 **Ba** 56	138.9 **La** 57	178.5 **Hf** 72	180.9 **Ta** 73	183.9 **W** 74	186.2 **Re** 75	190.2 **Os** 76	192.2 **Ir** 77	195.1 **Pt** 78	197.0 **Au** 79	200.6 **Hg** 80	204.4 **Tl** 81	207.2 **Pb** 82	209.0 **Bi** 83	209 **Po** 84	210 **At** 85	222 **Rn** 86	P
n=7	223 **Fr** 87	226.0 **Ra** 88	227.0 **Ac** 89	261 **Rf** 104	262 **Db** 105	263 **Sg** 106	262 **Bh** 107	265 **Hs** 108	266 **Mt** 109	269 **Unn** 110	272 **Uuu** 111	277 **Uub** 112		289 **Uuq** 114		289 **Uuh** 116		293 **Uuo** 118	

f-orbital elements

140.1 **Ce** 58	140.9 **Pr** 59	144.2 **Nd** 60	145 **Pm** 61	150.4 **Sm** 62	152.0 **Eu** 63	157.3 **Gd** 64	158.9 **Tb** 65	162.5 **Dy** 66	164.9 **Ho** 67	167.3 **Er** 68	168.9 **Tm** 69	173.0 **Yb** 70	175.0 **Lu** 71
232.0 **Th** 90	231 **Pa** 91	238.0 **U** 92	237.0 **Np** 93	244 **Pu** 94	243 **Am** 95	247 **Cm** 96	247 **Bk** 97	251 **Cf** 98	252 **Es** 99	257 **Fm** 100	258 **Md** 101	259 **No** 102	262 **Lw** 103

Fig. 3.2 Periodic table of elements. For each element, its symbol, atomic number, and atomic weight are shown

Fig. 3.3 Illustration of the physical states of water: (**a**) gas also known as water vapor, (**b**) liquid or common water, (**c**) solid also known as snow or ice

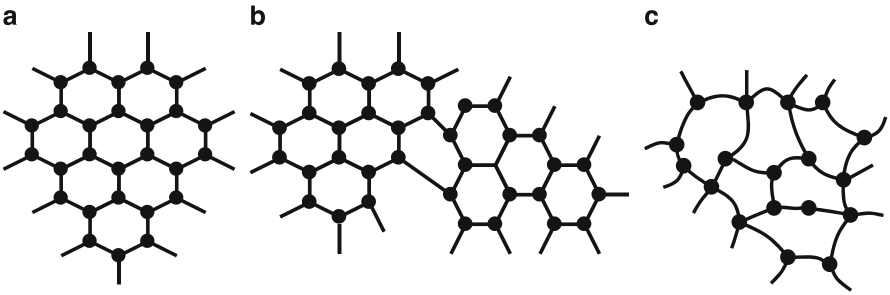


Fig. 3.4 Arrangement of atoms: (**a**) a single crystalline, (**b**) a polycrystalline, and (**c**) an amorphous material

atomic spacings. Materials in this state do not have the lowest possible internal energy but are stable, being in so-named local thermal equilibrium. These are polycrystalline materials.

There exist, however, solid materials which never reach their equilibrium condition, e.g., glasses or amorphous materials. Molten glass is very viscous and its constituent atoms cannot come into a periodic order (reach equilibrium condition) rapidly enough as the mass cools. Glasses have a higher energy content than the corresponding crystals and can be considered as a frozen, viscous liquid. There is no periodicity in the arrangement of atoms (the periodicity is of the same size as the atomic spacing) in the amorphous material. Amorphous solids or glass have the same properties in all directions (they are isotropic), like gases and liquids.

Therefore, the elements and their compounds in a solid state, including silicon, can be classified as single crystalline, polycrystalline, or amorphous materials. The differences among these classes of solids are shown schematically for a two-dimensional arrangement of atoms in Fig. 3.4.

3.2 Crystal Lattices and the Seven Crystal Systems

Now we are going to focus our discussion on crystals and their structures. A crystal can be defined as a solid consisting of a pattern that repeats itself periodically in all three dimensions. This pattern can consist of a single atom, group of atoms, or other

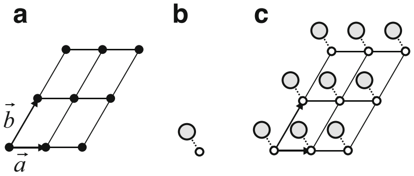


Fig. 3.5 Example of (**a**) two-dimensional lattice, (**b**) pattern, and (**c**) two-dimensional crystal illustrating a pattern associated with each lattice point

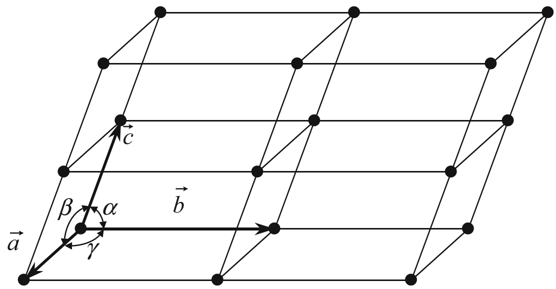


Fig. 3.6 Example of a three-dimensional lattice, with translation vectors and the angles between two vectors. By taking the origin at one lattice point, the position of any lattice point can be determined by a vector which is the sum of integer numbers of translation vectors

compounds. The periodic arrangement of such patterns in a crystal is represented by a lattice. A lattice is a mathematical object which consists of a periodic arrangement of points in all directions of space. One pattern is located at each lattice point. An example of a two-dimensional lattice is shown in Fig 3.5a. With the pattern shown in Fig. 3.5b, one can obtain the two-dimensional crystal in Fig. 3.5c which shows that a pattern is associated with each lattice point.

A lattice can be represented by a set of translation vectors as shown in the two-dimensional (vectors $\vec{a}$, $\vec{b}$) and three-dimensional lattices (vectors $\vec{a}$, $\vec{b}$, $\vec{c}$) in Fig. 3.6a, c, respectively. The lattice is invariant after translations through any of these vectors or any sum of an integer number of these vectors. When an origin point is chosen at a lattice point, the position of all the lattice points can be determined by a vector which is the sum of integer numbers of translation vectors. In other words, any lattice point can generally be represented by a vector $\vec{R}$ such that:

$$\begin{aligned} \vec{R} &= n_1 \vec{a} + n_2 \vec{b} + n_3 \vec{c}, \\ n_{1,2,3} &= 0, \pm 1, \pm 2, \ldots \end{aligned} \tag{3.1}$$

where $\vec{a}$, $\vec{b}$, $\vec{c}$ are the chosen translation vectors and the numerical coefficients are integers.

All possible lattices can be grouped in the seven crystal systems shown in Table 3.1, depending on the orientations and lengths of the translation vectors. No crystal may have a structure other than one of those in the seven classes shown in Table 3.1.

Table 3.1 The seven crystal systems

Crystal systems	Axial lengths and angles
Cubic	Three equal axes at right angles $a = b = c$, $\alpha = \beta = \gamma = 90°$
Tetragonal	Three axes at right angles, two equal $a = b \neq c$, $\alpha = \beta = \gamma = 90°$
Orthorhombic	Three unequal axes at right angles $a \neq b \neq c$, $\alpha = \beta = \gamma = 90°$
Trigonal	Three equal axes, equally inclined $a = b = c$, $\alpha = \beta = \gamma = 90°$
Hexagonal	Two equal coplanar axes at 120°, third axis at right angles $a = b \neq c$, $\alpha = \beta = 90°$, $\gamma = 120°$
Monoclinic	Three unequal axes, one pair not at right angles $a \neq b \neq c$, $\alpha = \gamma = 90° \neq \beta$
Triclinic	Three unequal axes, unequally inclined and none at right angles $a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90°$

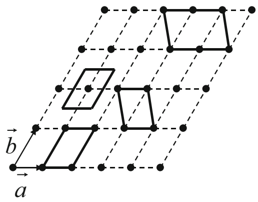


Fig. 3.7 Three examples of possible unit cells for a two-dimensional lattice The unit cells are delimited in solid lines. The same principle can be applied for the choice of a unit cell in three dimensions

A few examples of cubic crystals include Al, Cu, Pb, Fe, NaCl, CsCl, C (diamond form), Si, and GaAs; tetragonal crystals include In, Sn, and TiO_2; orthorhombic crystals include S, I, and U; monoclinic crystals include Se and P; triclinic crystals include $KCrO_2$; trigonal crystals include As, B, and Bi; and hexagonal crystals include Cd, Mg, Zn, and C (graphite form) (Fig. 3.6).

3.3 The Unit Cell Concept

A lattice can be regarded as a periodic arrangement of identical cells offset by the translation vectors mentioned in the previous section. These cells fill the entire space with no void. Such a cell is called a unit cell.

Since there are many different ways of choosing the translation vectors, the choice of a unit cell is not unique and all the unit cells do not have to have the same volume (area). Figure 3.7 shows several examples of unit cells for a two-dimensional lattice. The same principle can be applied when choosing a unit cell for a three-dimensional lattice.

The unit cell which has the smallest volume is called the primitive unit cell. A primitive unit cell is such that every lattice point of the lattice, without exception, can be represented by a vector such as the one in Fig. 3.7. An example of primitive unit cell in a three-dimensional lattice is shown in Fig. 3.6. The vectors defining the unit cell, $\vec{a}$, $\vec{b}$, $\vec{c}$, are basis lattice vectors of the primitive unit cell.

The choice of a primitive unit cell is not unique either, but all possible primitive unit cells are identical in their properties: they have the same volume, and each

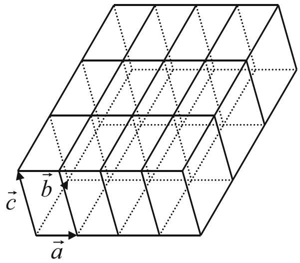


Fig. 3.8 Three-dimensional lattice and a corresponding primitive unit cell defined by the three basis vectors $\vec{a}$, $\vec{b}$, $\vec{c}$

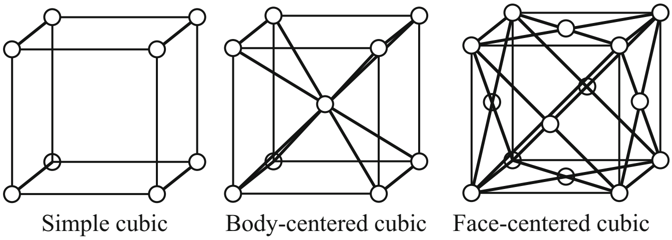


Fig. 3.9 Three-dimensional unit cells: simple cubic (left), body-centered cubic (bcc) (middle), and face-centered cubic (fcc) (right)

contains only one lattice point. The volume of a primitive unit cell is found from vector algebra:

$$V = \left| \vec{a} \cdot \left(\vec{b} \times \vec{c} \right) \right| \quad (3.2)$$

The number of primitive unit cells in a crystal, N, is equal to the number of atoms of a particular type, with a particular position in the crystal, and is independent of the choice of the primitive unit cell:

$$\text{Primitive unit cell volume} = \frac{\text{Crystal volume}}{N}$$

A primitive unit cell is in many cases characterized by non-orthogonal lattice vectors (as in Fig. 3.8). As one likes to visualize the geometry in orthogonal coordinates, a conventional unit cell (but not necessarily a primitive unit cell) is often used. In most semiconductor crystals, such a unit cell is chosen to be a cube, whereas the primitive cell is a parallelepiped and is more convenient to use due to its more simple geometrical shape.

A conventional unit cell may contain more than one lattice point. To illustrate how to count the number of lattice points in a given unit cell, we will use Fig. 3.9 which depicts different cubic unit cells.

In our notations n_i is the number of points in the interior, n_f is the number of points on faces (each n_f is shared by two cells), and n_c is the number of points on corners

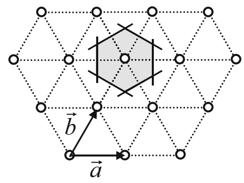


Fig. 3.10 Two-dimensional Wigner-Seitz cell and its construction method: select a lattice point, draw lines from a given lattice point to all nearby points, bisect these lines with orthogonal planes, and construct the smallest polyhedron that contains the first selected lattice

(each n_c point is shared by eight corners). For example, the number of atoms per unit cell in the fcc lattice (Fig. 3.9c) ($n_i = 0$, $n_f = 6$, and $n_c = 8$) is:

$$n_u = n_i + \frac{n_f}{2} + \frac{n_c}{8} = 4 \text{ atoms/unit cell} \tag{3.3}$$

3.4 The Wigner-Seitz Cell

The primitive unit cell that exhibits the full symmetry of the lattice is called Wigner-Seitz cell. As it is shown in Fig. 3.10, the Wigner-Seitz cell is formed by (1) drawing lines from a given Bravais lattice point to all nearby lattice points, (2) bisecting these lines with orthogonal planes, and (3) constructing the smallest polyhedron that contains the selected point. This construction has been conveniently shown in two dimensions but can be continued in the same way in three dimensions. Because of the method of construction, the Wigner-Seitz cell translated by all the lattice vectors will exactly cover the entire lattice.

3.5 Bravais Lattices

Because a three-dimensional lattice is constituted of unit cells which are translated from one another in all directions to fill up the entire space, there exist only 14 different such lattices. They are illustrated in Fig. 3.11 and each is called a Bravais lattice after the name of Bravais (1848).

In the same manner, as no crystal may have a structure other than one of those in the seven classes shown in Fig. 3.11, no crystal can have a lattice other than one of those 14 Bravais lattices.

3.6 Point Groups

Because of their periodic nature, crystal structures are brought into self- coincidence under a number of symmetry operations. The simplest and most obvious symmetry operation is translation. Such an operation does not leave any point of the lattice

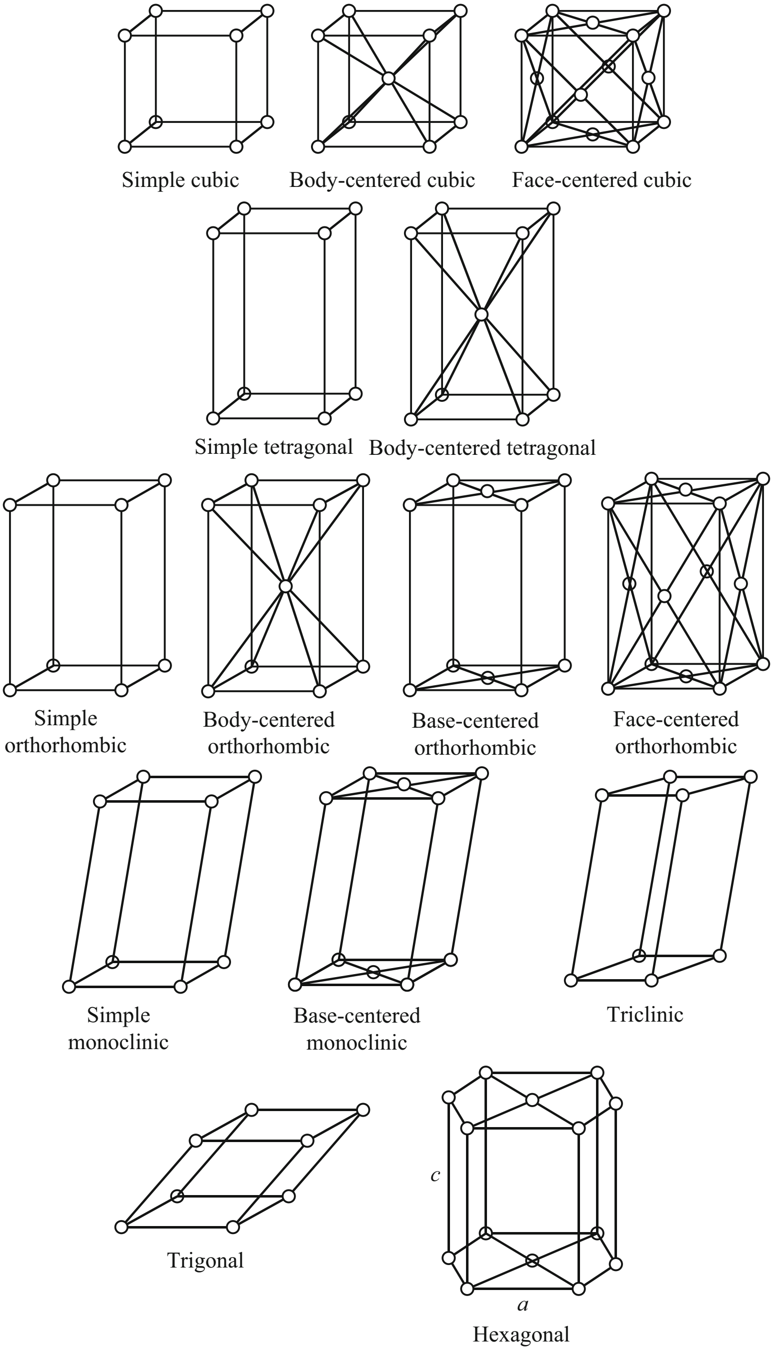


Fig. 3.11 The 14 Bravais lattices, illustrating all the possible three-dimensional crystal lattices

invariant. There exists another type of symmetry operation, called point symmetry, which leaves a point in the structure invariant. All the point symmetry operations can be classified into mathematical groups called point groups, which will be reviewed in this section.

The interested reader is referred to mathematics texts on group theory for a complete understanding of the properties of mathematical groups. For the scope of the discussion here, one should simply know that a mathematical group is a collection of elements which can be combined with one another and such that the result of any such combination is also an element of the group. A group contains a neutral element such that any group element combined with it remains unchanged. For each element of a group, there also exists an inverse element in the group such that their combination is the neutral element.

3.6.1 C_s Group (Plane Reflection)

A plane reflection acts such that each point in the crystal is mirrored on the other side of the plane as shown in Fig. 3.12. The plane of reflection is usually denoted by σ. When applying the plane reflection twice, i.e., σ^2, we obtain the identity which means that no symmetry operation is performed. The reflection and the identity form the point group which is denoted C_s and which contains only these two symmetry operations (Fig. 3.13).

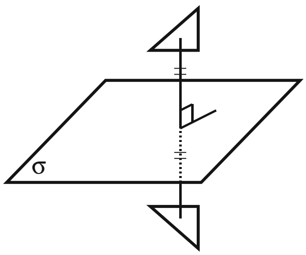


Fig. 3.12 Illustration of a plane reflection. The triangular object and its reflected image are mirror images of each other

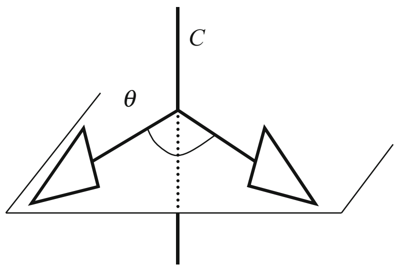


Fig. 3.13 Illustration of rotation symmetry. The triangular object and its image are separated by an angle equal to θ

3.6.2 C_n Groups (Rotation)

A rotation about an axis and through an angle θ (n is an integer) is such that any point and its image are located in a plane perpendicular to the rotation axis and the in-plane angle that they form is equal to θ, as shown in Fig. 3.14. In crystallography, the angle of rotation cannot be arbitrary but can only take the following fractions of 2π: $\theta = \frac{2\pi}{1}$, $\frac{2\pi}{2}$, $\frac{2\pi}{3}$, $\frac{2\pi}{4}$, $\frac{2\pi}{6}$.

It is thus common to denote as C_n a rotation through an angle $\frac{2\pi}{n}$ where n is an integer equal to 1, 2, 3, 4, or 6. The identity or unit element corresponds to $n = 1$, i.e., C_1. For a given axis of rotation and integer n, a rotation operation can be repeated, and this actually leads to n rotation operations about the same axis, corresponding to the n allowed angles of rotation: $1 \times \frac{2\pi}{n}$, $2 \times \frac{2\pi}{n}$, …, $(n-1) \times \frac{2\pi}{n}$, and $n \times \frac{2\pi}{n}$. These n rotation operations, which include the identity, form a group also denoted C_n.

One says that the C_n group consists of n-fold symmetry rotations, where n can be equal to 1, 2, 3, 4, or 6. Figure 3.14 depicts the perspective view of the crystal bodies with symmetries C_1, C_2, C_3, C_4, C_6. The rotations are done so that the elbow pattern coincides with itself. It is also common to represent these symmetry groups with the rotation axis perpendicular to the plane of the figure, as shown in Fig. 3.15.

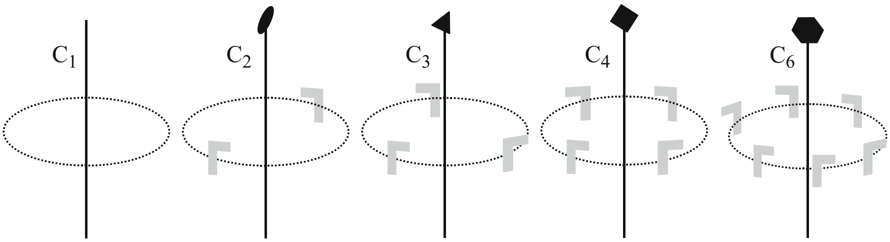


Fig. 3.14 Crystal bodies with symmetries C_1, C_2, C_3, C_4, and C_6. The elbow patterns are brought into self-coincidence after a rotation around the axis shown and through an angle equal to $2\pi/n$ where $n = 1, 2, 3, 4$, or 6

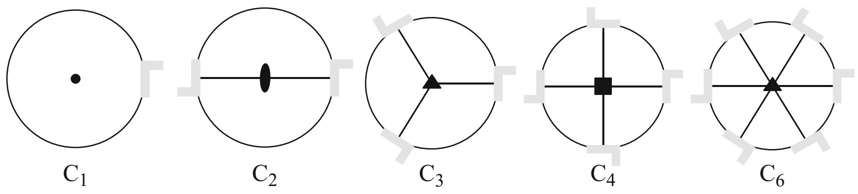


Fig. 3.15 Crystal bodies with symmetries C_1, C_2, C_3, C_4, and C_6 with the rotation axes perpendicular to the plane of the figure

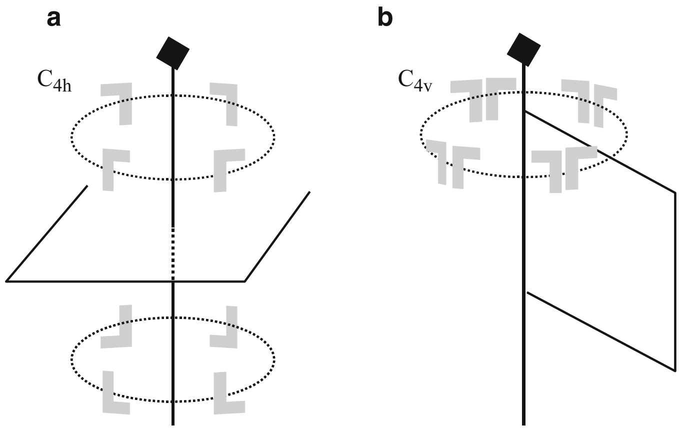


Fig. 3.16 Crystal bodies with symmetries (**a**) C_{4h} where the reflection plane is perpendicular to the rotation axis and (**b**) C_{4v} where the reflection plane passes through the rotation axis

3.6.3 C_{nh} and C_{nv} Groups

When combining a rotation of the C_n group and a reflection plane σ, the axis of rotation is usually chosen vertical. The reflection plane can either be perpendicular to the axis and then be denoted σ_h (horizontal) or pass through this axis and then be denoted σ_v (vertical). All the possible combinations of such symmetry operations give rise to two types of point groups: the C_{nh} and the C_{nv} groups.

The C_{nh} groups contain an n-fold rotation axis C_n and a plane σ_h perpendicular to it. (a) Shows the bodies with a symmetry C_{4h}. The number of elements in a C_{nh} group is $2n$.

The C_{nv} groups contain an n-fold axis C_n and a plane σ_v passing through the rotation axis. Figure 3.16b shows the bodies with a symmetry C_{4v}. The number of elements is $2n$ too.

3.6.4 D_n Groups

When combining a rotation of the C_n group and a C_2 rotation with an axis perpendicular to the first rotation axis, this gives rise to a total of n C_2 rotation axes. All the possible combinations of such symmetry operations give rise to the point groups denoted D_n. The number of elements in this point group is $2n$. For example, the symmetry operations in D_4 are illustrated in Fig. 3.17.

3.6.5 D_{nh} and D_{nd} Groups

When combining an element of the C_{nh} group and a C_2 rotation which has an axis perpendicular to the C_n axis, this gives also rise to a total of n C_2 rotation axes. All

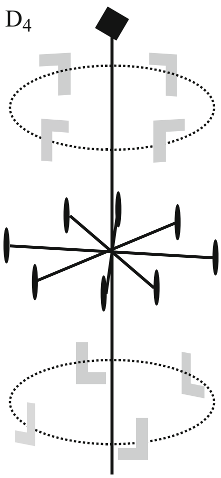


Fig. 3.17 Crystal bodies with symmetry D_4. In addition to the C_4 axis, there are four C_2 axes of rotation perpendicular to the C_n axis

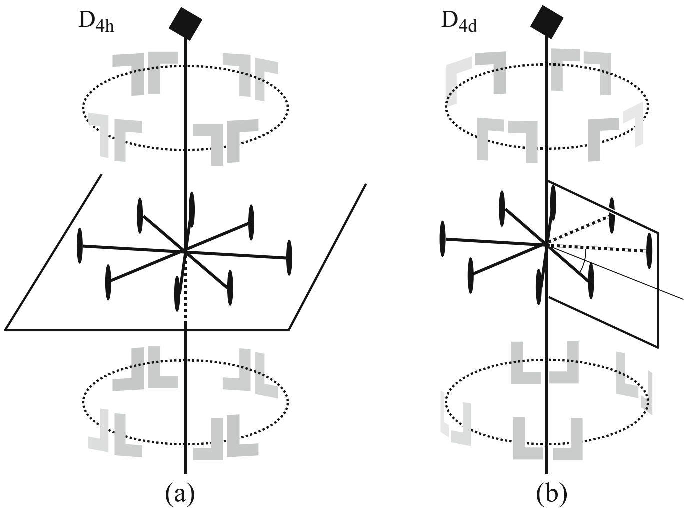


Fig. 3.18 Bodies with symmetries (**a**) D_{4h} and (**b**) D_{4d}

the possible combinations of such symmetry operations lead to the point group denoted D_{nh}. This point group can also be viewed as the result of combining an element of the D_n group and a σ_h (horizontal) reflection plane. This group can also be viewed as the result of combining an element of the D_n group and n σ_v (vertical) reflection planes which pass through both the C_n and the n C_2 axes.

The number of elements in the D_{nh} point group is $4n$, as it includes the $2n$ elements of the D_n group, and all these $2n$ elements combined with a plane reflection σ_h. For example, the symmetry operations in D_{4h} are illustrated in Fig. 3.18a.

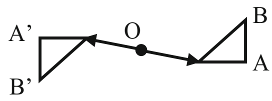


Fig. 3.19 Illustration of inversion symmetry. Any point of the triangular object and its image are such that the inversion center is at the middle of these two points

Now, when combining an element of the C_{nv} group and a C_2 rotation which has an axis perpendicular to the C_n axis and which is such that the σ_v (vertical) reflection planes bisect two adjacent C_2 axes, this leads to the point group denoted D_{nd}. This point group can also be viewed as the result of combining an element of the D_n group and n σ_v (vertical) reflection planes which bisect the C_2 axes.

The number of elements in the D_{nd} point group is $4n$ as well. For example, the symmetry operations in D_{4d} are illustrated in 3.18b.

3.6.6 C_i Group

An inversion symmetry operation involves a center of symmetry (e.g., O) which is at the middle of a segment formed by any point (e.g., A) and its image through inversion symmetry (e.g., A′), as shown in Fig. 3.19.

When applying an inversion symmetry twice, we obtain the identity which means that no symmetry operation is performed. The inversion and the identity form the point group which is denoted C_i and which contains only these two symmetry operations.

3.6.7 C_{3i} and S_4 Groups

When combining an element of the C_n group and an inversion center located on the axis of rotation, the symmetry operations get more complicated. If we consider the C_1 group (identity), we obtain the inversion symmetry group C_i. In the case of C_2 group, we get the plane reflection group C_s. And if we consider the C_6 group, we actually obtain the C_{3h} point group.

When we combine *independently* elements from the C_4 group and the inversion center, we get the C_{4h} point group. However, there is a subgroup of the C_{4h} point group which can be constructed by considering a new symmetry operation, the roto-inversion, which consists of a C_4 rotation immediately followed by an inversion through a center on the rotation axis. It is important to realize that the roto-inversion is a single symmetry operation, i.e., the rotation is not independent of the inversion. The subgroup is made by combining roto-inversion operation, is denoted S_4, and is illustrated in Fig. 3.20. Its number of elements is 4.

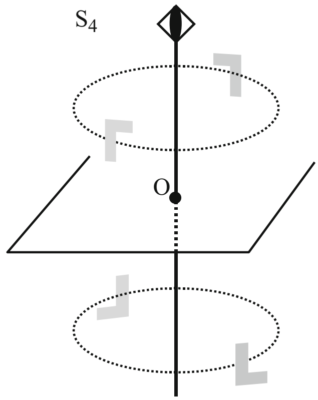


Fig. 3.20 Bodies with symmetry S_4

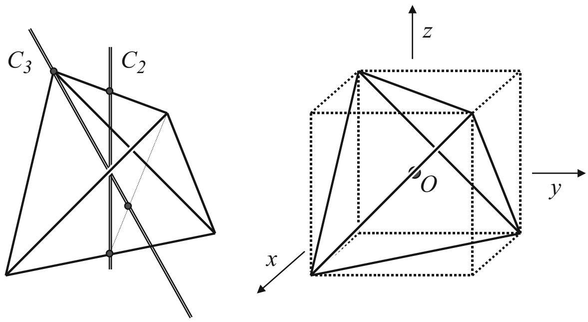


Fig. 3.21 Axes of rotation for the T group, including four C_3 and three C_2 axes. The orientation of the tetrahedron with respect to the cubic coordinate axes is shown on the right

A similar point group is obtained when considering roto-inversions from the C_3 group. The new point group is denoted C_{3i}.

3.6.8 *T* Group

The tetrahedron axes group T is illustrated in Fig. 3.21. It contains some of the symmetry operations which bring a regular tetrahedron into self-coincidence. The tetrahedron and its orientation with respect to the cubic coordinate axes are also shown.

The number of elements is 12, which includes:

- Rotations through an angle $\frac{2\pi}{3}$ or $\frac{4\pi}{3}$, about the four C_3 axes which are the body diagonals of a cube (yielding at total of eight elements)
- Rotations through an angle π, about the three C_2 axes $(\vec{x}, \vec{y}, \vec{z})$ passing through the centers of opposite faces (three elements)
- The identity (one element)

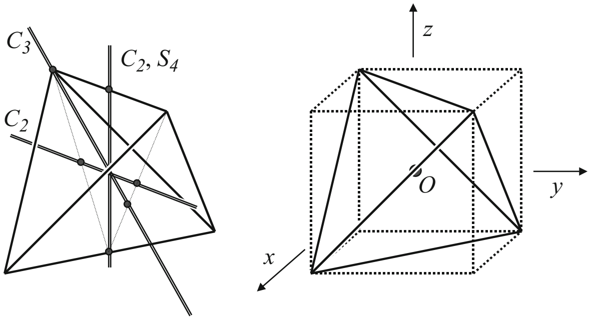


Fig. 3.22 Axes of rotation for T_d group, including four C_3, three C_2 axes passing through the center of opposite faces, three S_4 axes, and six C_2 axes passing through the centers of diagonally opposite sides

3.6.9 T_d Group

The T_d point group contains all the symmetry elements of a regular tetrahedron. Basically, it includes all the symmetry operations of the T group in addition to an inversion center at the center of the tetrahedron (Fig. 3.22).

The number of elements is 24, which includes:

- Rotations through an angle $\frac{2\pi}{3}$ or $\frac{4\pi}{3}$, about the four C_3 axes which are the body diagonals of a cube (yielding at total of eight elements)
- Rotations through an angle π, about the three C_2 axes $(\vec{x},\vec{y},\vec{z})$ passing through the centers of opposite faces (three elements)
- Rotations through an angle $\frac{\pi}{2}$ or $\frac{3\pi}{2}$ (S_4), about the three axes $(\vec{x},\vec{y},\vec{z})$ passing through the centers of opposite faces, followed by an inversion through the center point O of a cube, (six elements)
- Rotations through an angle π, about the six C_2 axes passing through the centers of diagonally opposite sides (in diagonal planes of a cube), followed by an inversion through the center point O (six elements)
- Finally, the identity (one element)

3.6.10 O Group

The cubic axes group O consists of rotations about all the symmetry axes of a cube. The number of elements is 24, which includes:

- Rotations through the angles $\frac{2\pi}{4}$, $\frac{4\pi}{4}$, or $\frac{6\pi}{4}$, about the three C_4 axes passing through the centers of opposite faces (yielding a total of nine elements)
- Rotations through the angles $\frac{2\pi}{3}$ or $\frac{4\pi}{3}$, about the four C_3 axes passing through the opposite vertices (eight elements)
- Rotations through an angle π, about the six C_2 axes passing through the midpoints of opposite edges (six elements)
- Finally, the identity (one element)

3.6.11 O_h Group

The O_h group includes the full symmetry of a cube in addition to an inversion symmetry. The number of elements is 48, which includes:

- All the symmetry operations of the O group (24 elements)
- And all the symmetry operations of the O group combined with an inversion through the body-centered point of a cube (24 elements).

3.6.12 List of Crystallographic Point Groups

The point groups previously reviewed are constructed by considering all the possible combinations of basic symmetry operations (plane reflections and rotations) discussed in subsections 3.6.1 to 3.6.11. By doing so, one would find that there exist only 32 crystallographic point groups. Crystallographers normally use two kinds of notations for these point symmetry groups. Table 3.2 shows the correspondence between two widely used notations.

3.7 Space Groups

The other type of symmetry in crystal structures, (translation symmetry), reflects the self-coincidence of the structure after the displacements through arbitrary lattice vectors ($\vec{R}$).

These symmetry operations are independent of the point symmetry operations as they do not leave a point invariant (except for the identity). The combination of translation symmetry and point symmetry elements gives rise to new symmetry operations which also bring the crystal structure into self-coincidence. An example of such new operation is a glide plane by which the structure is reflected through a reflection plane and then translated by a vector parallel to the plane.

With these new symmetry operations, a larger symmetry operation group is formed, called space group. There are only 230 possible three-dimensional crystallographic space groups which are conventionally labeled with a number from No. 1 to No. 230.

3.8 Directions and Planes in Crystals: Miller Indices

In order to establish the proper mathematical description of a lattice, we have to identify the directions and planes in a lattice. This is done in a crystal using Miller indices (hkl). We introduce Miller indices by considering the example shown in Fig. 3.23.

Table 3.2 List of the 32 crystallographic point groups

Crystal system	Schoenflies symbol	Hermann-Mauguin symbol
Triclinic	C_1	*1*
	C_i	$\bar{1}$
Monoclinic	C_2	*2*
	C_s	*m*
	C_{2h}	*2/m*
Orthorhombic	D_2	*222*
	C_{2v}	*mm2*
	D_{2h}	*mmm*
Tetragonal	C_4	*4*
	S_4	$\bar{4}$
	C_{4h}	*4/m*
	D_4	*422*
	C_{4v}	*4 mm*
	D_{2d}	$\bar{4}2m$
	D_{4h}	*4/mmm*
Cubic	T	*23*
	T_h	*m3*
	O	*432*
	T_d	$\bar{4}3m$
	O_h	*m3m*
Trigonal	C_3	*3*
	C_{3i}	$\bar{3}$
	D_3	*32*
	C_{3v}	*3m*
	D_{3d}	$\bar{3}m$
Hexagonal	C_6	*6*
	C_{3h}	$\bar{6}$
	C_{6h}	*6/m*
	D_6	*622*
	C_{6v}	*6 mm*
	D_{3h}	$\bar{6}$
	D_{6h}	*6/mmm*

Figure 3.23 shows a crystal plane which passes through lattice points and intersects the axes: $2a$, $3b$, $2c$, where $\vec{a}$, $\vec{b}$, $\vec{c}$ are basic lattice vectors. To obtain Miller indices, we form the ratio $\frac{1}{2}:\frac{1}{3}:\frac{1}{2}$ and put the fractions on the smallest common denominator. The Miller indices are the corresponding numerators. Thus we obtain the Miller indices for the plane: $(hkl) = (323)$.

It also follows that a lattice plane with Miller indices *(hkl)* will be intersected by the axis $\vec{a}$, $\vec{b}$, $\vec{c}$ at distances $\frac{Na}{h}, \frac{Nb}{k}, \frac{Nc}{l}$ where N is an integer. The Miller indices for

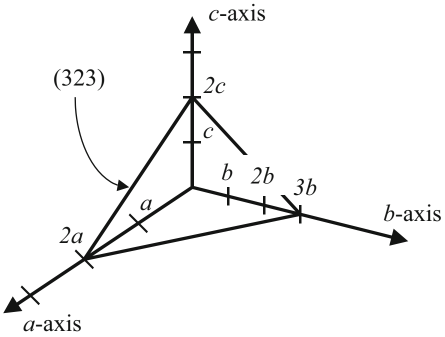


Fig. 3.23 Example of a plane which passes through lattice points. Its Miller indices are (*hkl*) = (323) and are used to identify this plane in the crystal. These indices are obtained as follows: note where the plane intersects the coordinate axes, it is either an integer multiple or an irreducible fraction of the axis unit length; invert the intercept values; using the appropriate multiplier, convert these inverted values into integer numbers; and enclose the integer numbers in parenthesis

Table 3.3 Conventions used to label directions and planes in crystallography

Notation	Designation
(*hkl*)	Plane
{*hkl*}	Equivalent plane
[*uvw*]	Direction
<*uvw*>	Equivalent direction
(*hkil*)	Plane in hexagonal systems
[*uvtw*]	Direction in hexagonal systems

a few planes in a cubic lattice are shown in Fig. 3.23. These Miller indices are obtained as described above and by using $\frac{1}{1}, \frac{1}{\infty}, \frac{1}{\infty} = 1{:}0{:}0 = (100)$.

For a crystal plane that intersects the origin, one typically has to determine the Miller indices for an equivalent plane which is obtained by translating the initial plane by any lattice vector. The conventions used to label directions and planes in crystallographic systems are summarized in Table 3.3.

The notation for the direction of a straight line passing through the origin is [*uvw*], where *u*, *v*, and *w* are the three smallest integers whose ratio *u*:*v*:*w* is equal to the ratio of the lengths (in units of *a*, *b*, and *c*) of the components of a vector directed along the straight line. For example, the symbol for the *a*-axis in Fig. 3.23, which coincides with vector $\vec{a}$, is [100].

For the indices of both plane and directions, a negative value of the index is written with a bar sign above the index, such as $(\bar{h}kl)$ or $[u\bar{v}w]$.

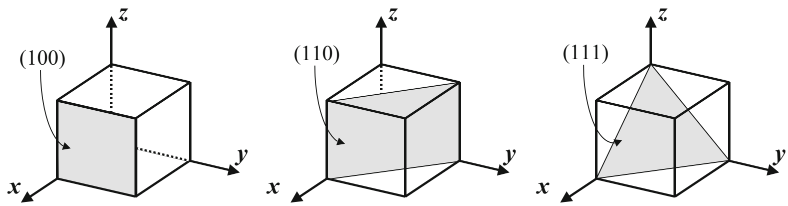
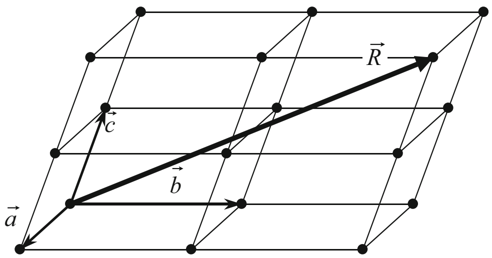


Fig. 3.24 Miller indices of the three principal planes in the cubic structure. If a plane is parallel to an axis, we consider that it "intersects" this axis at infinity and we get the Miller indices: 1,∞,∞ = > 1/1:1/∞:1/∞=1:0:0 = > (100)

Example

Q Determine the direction index for the lattice vector shown below.



A We can decompose the vector $\vec{R}$ as: $\vec{R} = 1\,\vec{a} + 2\,\vec{b} + 2\,\vec{c}$. This corresponds to $u = 1$, $v = 2$, $w = 2$, and the direction is thus [122].

In cubic systems, such as simple cubic, body-centered cubic, and face-centered cubic lattices, the axes of Fig. 3.24 are chosen to be orthonormal, i.e., the unit vectors are chosen orthogonal and of the same length equal to the side of the cubic unit cell. The axes are then conventionally denoted *x*, *y*, and *z* instead of *a*, *b*, and *c*, as shown in Fig. 3.24.

In addition, for cubic systems, the Miller indices for directions and planes have the following particular and important properties:

- The direction denoted [*hkl*] is perpendicular to plane denoted (*hkl*).
- The interplanar spacing is given by the following expression and is shown in the example in Fig. 3.25:

$$d_{hkl} = a/\sqrt{h^2+k^2+l^2} \tag{3.4}$$

- The angle θ between two directions $[h_1k_1l_1]$ and $[h_2k_2l_2]$ is given by the relation:

$$\cos(\theta) = (h_1h_2+k_1k_2+l_1l_2)\Big/\sqrt{\left(h_1^2+k_1^2+l_1^2\right)\left(h_2^2+k_2^2+l_2^2\right)} \tag{3.5}$$

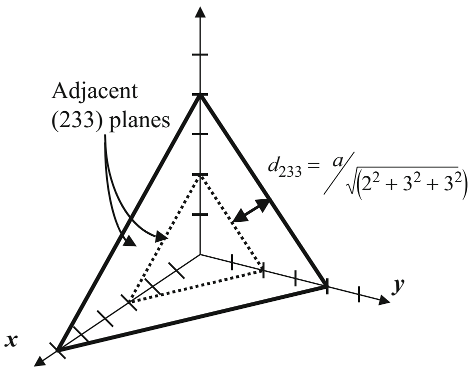


Fig. 3.25 Illustration of the interplanar spacing in a cubic lattice between two adjacent (233) planes

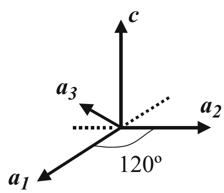
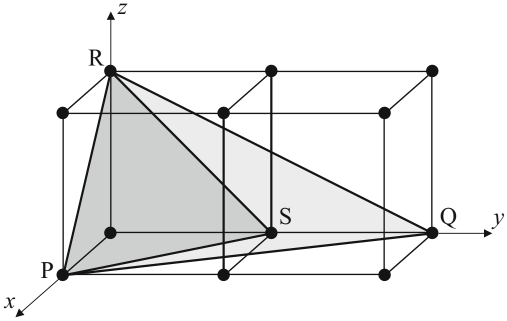


Fig. 3.26 Coordinate axes used to determine Miller indices for hexagonal systems

Example

Q Determine the angle between the two planes shown below (PSR) and (PQR), in a cubic lattice.



A The Miller indices for the (PSR) plane are (111), while they are (212) for the (PQR) plane. The angle θ between these two planes is given by the following cosine function: $\cos(\theta) = \frac{1\times2+1\times1+1\times2}{\sqrt{(1^2+1^2+1^2)(2^2+1^2+2^2)}} = \frac{5\sqrt{3}}{9}$.

The angle between the two planes is therefore 15.8 deg.

In hexagonal systems, the *a*- and *b*-axes of Fig. 3.26 are chosen in the plane formed by the base of the hexagonal unit cell and form a 120 degree angle. They are denoted $\vec{a}_1$ and $\vec{a}_2$ and their length is equal to the side of the hexagonal base. The unit

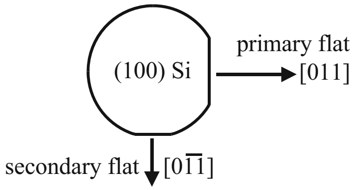


Fig. 3.27 Illustration of the use of primary and secondary flats on a (100) oriented silicon crystal wafer to indicate the in-plane crystallographic orientation of the wafer

vector perpendicular to the base is still denoted c. In addition, it is also conventional to introduce a (redundant) fourth unit vector denoted $\vec{a}_3$ in the base plane and equal to $-(\vec{a}_1 + \vec{a}_2)$, as shown in Fig. 3.26. It is then customary to use a four-index system for planes and directions: ($hkil$) and [$uvtw$], respectively, as shown in Fig. 3.26. The additional index that is introduced for hexagonal systems is such that $i = -(h + k)$ and $t = -(u + v)$, which is a direct consequence of the choice of the fourth unit vector $\vec{a}_3$.

In modern microelectronics, it is often important to know the in-plane crystallographic directions of a wafer and this can be accomplished using Miller indices. During the manufacturing of the circular wafer disk, it is common to introduce a "flat" to indicate a specific crystal direction. To illustrate this, let us consider the (100) oriented silicon wafer shown in Fig. 3.27. A primary flat is such that it is perpendicular to the [011] direction, while a smaller secondary flat is perpendicular to the [01$\bar{1}$] direction.

3.9 Real Crystal Structures

Most semiconductor solids crystallize into a few types of structures which are discussed in this section. They include the diamond, zinc blende, sodium chloride, cesium chloride, hexagonal close-packed, and wurtzite structures.

3.9.1 Diamond Structure

Elements from the column *IV* in the periodic table, such as carbon (the diamond form), germanium, silicon, and gray tin, crystallize in the diamond structure. The Bravais lattice of diamond is face-centered cubic. The basis has two identical atoms located at (0,0,0) and (¼,¼,¼) in the cubic unit cell, for each point of the fcc lattice. The point group of diamond is O_h. The lattice constants are $a = 3.56$, 5.43, 6.65, and 6.46 Å for the four crystals mentioned previously in the same order. The conventional cubic unit cell thus contains eight atoms. There is no way to choose a primitive unit cell such that the basis of diamond contains only one atom.

The atoms which are at least partially in the conventional cubic unit cell are located at the following coordinates: (0,0,0), (0,0,1), (0,1,0), (1,0,0), (1,1,0), (1,0,1), (0,1,1), (1,1,1), (½,½,0), (0,½,½), (½,0,½), (½,½,1), (1,½,½), (½,1,½), (¼,¼,¼), (¾,¾,¼), (¾,¼,¾), and (¼,¾,¾).

The tetrahedral bonding characteristic of the diamond structure is shown in Fig. 3.28a. Each atom has 4 nearest neighbors and 12 s nearest neighbors. For example, the atom located at (¼,¼,¼) at the center of the cube in Fig. 3.28b has four

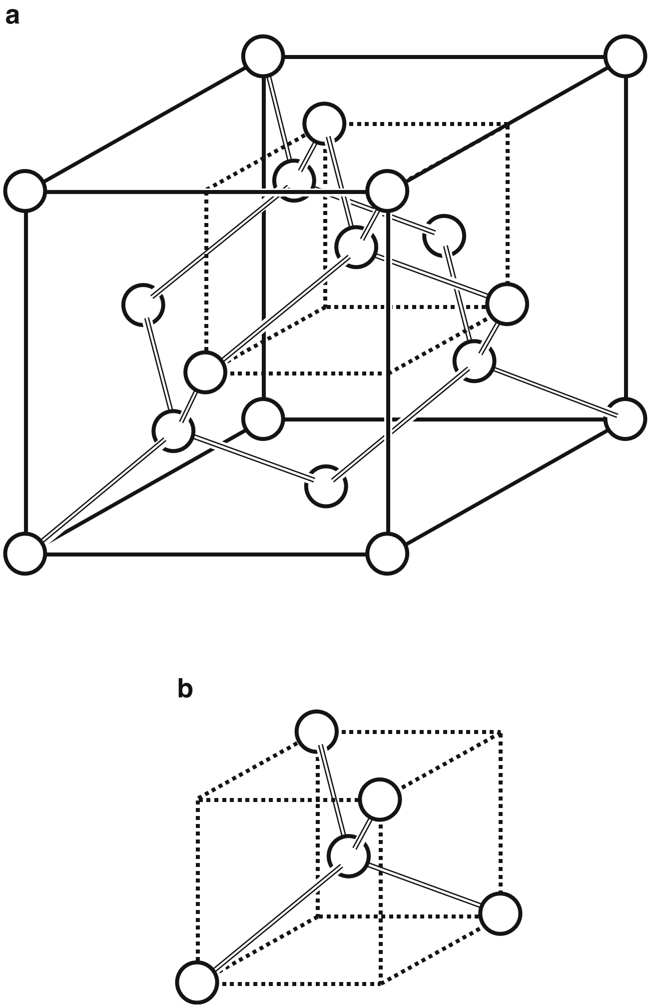


Fig. 3.28 (**a**) Diamond lattice. The Bravais lattice is face-centered cubic with a basis consisting of two identical atoms displaced from each other by a quarter of the cubic body diagonal. The atoms are connected by covalent bonds. The cube outlined by the dashed lines shows one tetrahedral unit. (**b**) Tetrahedral unit of the diamond lattice

nearest neighbors also shown in Fig. 3.28b which are located at (0,0,0), (½,½,0), (0,½,½), and (½,0,½).

The number of atoms/unit cell for the diamond lattice is found from $n_i = 4$, $n_f = 6$, and $n_c = 8$ where n_i, n_f, and n_c are the numbers of points in the interior, on faces, and on corners of the cubic unit cell shown in Fig. 3.28a, respectively. Note that each of the n_f points is shared between two cells and each of the n_c points is shared between eight cells. Therefore: $n_u = 4 + \frac{6}{6} + \frac{8}{8} = 8$ atoms/unit cell. The atomic density or the number of atoms per cm^3, n, is given by $n = \frac{n_u}{a^3}$ atoms/unit cell. For example, for silicon, we have $a = 5.43$ Å, and $n = 8/(0.543 \times 10^{-7})^3 = 5 \times 10^{22}$ atoms/cm^3.

3.9.2 Zinc Blende Structure

The most common crystal structure for III–V compound semiconductors, including GaAs, GaSb, InAs, and InSb, is the sphalerite or zinc blende structure shown in Fig. 3.29. The point group of the zinc blende structure is T_d.

The zinc blende structure has two different atoms. Each type of atom forms a face-centered cubic lattice. Each atom is bounded to four atoms of the other type. The sphalerite structure as a whole is treated as a face-centered cubic Bravais lattice with a basis of two atoms displaced from each other by $(a/4)(x + y + z)$, i.e., one fourth of the length of a body diagonal of the cubic lattice unit cell. Some important properties of this crystal result from the fact that the structure does not appear the same when viewed along a body diagonal from one direction and then the other. Because of this, the sphalerite structure is said to lack inversion symmetry. The crystal is therefore polar in its <111> directions, i.e., the [111] and the $[\bar{1}\bar{1}\bar{1}]$ directions are not equivalent. When both atoms are the same, the sphalerite structure has the diamond structure, which has an inversion symmetry and was discussed previously.

In the case of GaAs, for example, the solid spheres in Fig. 3.29 represent Ga atoms and the open spheres represent As atoms. Their positions are:

Ga: (0,0,0), (½,½,0), (0,½,½), (½,0,½), (½,1,½), (½,½,1), (1,½,½)
As: (¼,¼,¼), (¾,¾,¼), (¾,¼,¾), (¼,¾,¾)

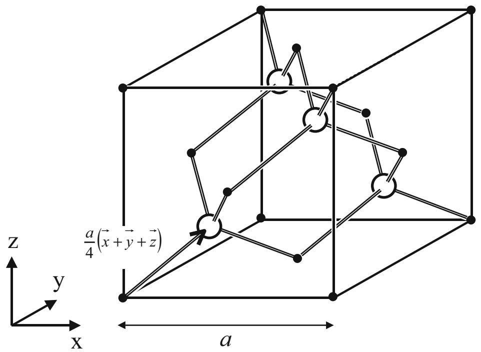


Fig. 3.29 Cubic unit cell for the zinc blende structure. The Bravais lattice is face-centered cubic with a basis of two different atoms represented by the open and solid spheres and separated by a quarter of the cubic body diagonal. The crystal does not appear the same when viewed along a body diagonal from one direction or the other

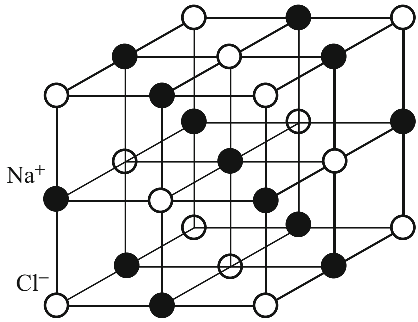


Fig. 3.30 Sodium chloride crystal. The Bravais lattice is face-centered cubic with a basis of two ions: one Cl^- ion at (0,0,0) and one Na^+ ion at (½,½,½), separated by one half of the cubic body diagonal. The figure shows one cubic unit cell

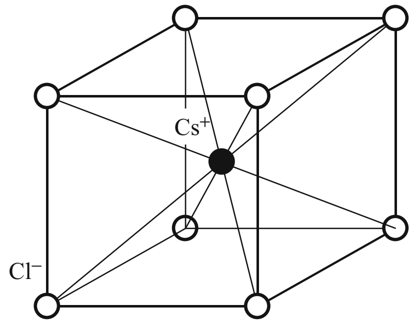


Fig. 3.31 The cesium chloride crystal structure. The Bravais lattice is cubic with a basis of two ions: one Cl^- ion at (0,0,0) and one Cs^+ ion at (½,½,½), separated by one half the cubic body diagonal

3.9.3 Sodium Chloride Structure

The structure of sodium chloride, NaCl, is shown in Fig. 3.30. The Bravais lattice is face-centered cubic and the basis consists of one Na atom and one Cl atom separated by one half the body diagonal of the cubic unit cell. The point group of the sodium chloride structure is O_h.

There are four units of NaCl in each cubic unit cell, with atoms in the positions:

Cl: (0,0,0), (½,½,0), (½,0, ½), (0, ½,½)
Na: (½,½,½), (0,0, ½), (0, ½,0), (½,0,0)

3.9.4 Cesium Chloride Structure

The cesium chloride structure is shown in Fig. 3.31. The Bravais lattice is simple cubic and the basis consists of two atoms located at the corner (0,0,0) and center positions (½,½,½) of the cubic unit cell. Each atom may be viewed as at the center of a cube of atoms of the opposite kind, so that the number of nearest neighbors or coordination number is eight. The point group of the cesium chloride structure is T_d.

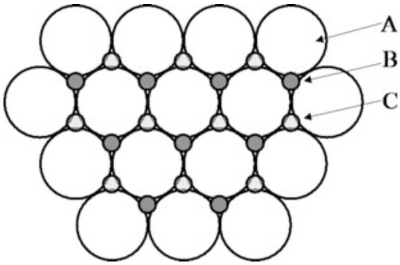
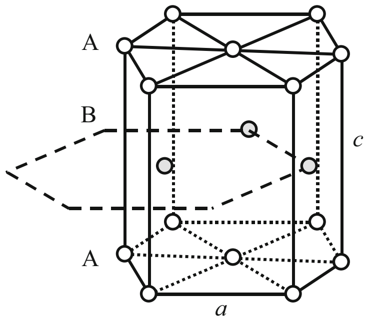


Fig. 3.32 The closed-packed array of spheres. Note the three different possible positions, A, B, and C for the successive layers. The most space-efficient way to arrange identical spheres or atoms in a plane is to first place each sphere in contact with six others in that plane (positions A). The most stable way to stack a second layer of such spheres is by placing each one of them in contact with three spheres of the bottom layer (positions B). The third stable layer can then either be such that the spheres occupy positions above A or C

Fig. 3.33 The hexagonal close-packed (hcp) structure. This Bravais lattice of this structure is hexagonal, with a basis of two identical atoms. It is constructed by stacking layers in the ABABAB... sequence. The lattice parameters a and c are indicated



3.9.5 Hexagonal Close-Packed Structure

The simplest way to stack layers of spheres is to place centers of spheres (atoms) directly above one another. The resulting structure is called a *simple hexagonal structure*. There is, in fact, no example of crystals with this structure because it is unstable. However, spheres can be arranged in a single hexagonal close-packed layer A (Fig. 3.32) by placing each sphere in contact with six others. A second similar layer B may be added by placing each sphere of B in contact with three spheres of the bottom layer, at positions B in Fig. 3.32. This arrangement has the lowest energy and is therefore stable. A third layer may be added in two different ways. We obtain the cubic structure if the spheres of the third layer C are added over the holes in the first layer A that are not occupied by B, as in Fig. 3.32. We obtain the hexagonal close-packed structure (Fig. 3.33) when the spheres in the third layer are placed directly over the centers of the spheres in the first layer, thus replicating layer A. The Bravais lattice is hexagonal. The point group of the hexagonal close-packed structure is D_{6h}. The fraction of the total volume occupied by the spheres is 0.74 for both structures (see Problems).

Table 3.4 c/a parameter for various hexagonal crystals

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

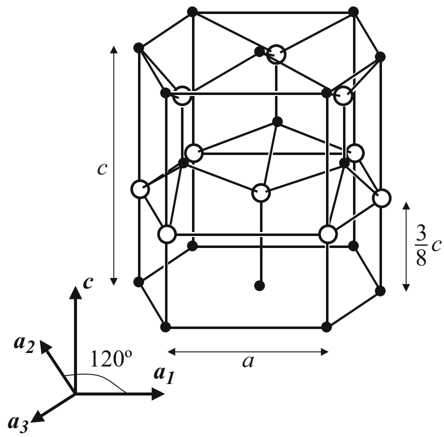


Fig. 3.34 The wurtzite structure consists of two interpenetrating hcp structures, each with a different atom, shifted along the c-direction. The bonds between atoms and the hexagonal symmetry are shown

Zinc, magnesium, and low-temperature form of titanium have the hcp structure. The ratio *c/a* for ideal hexagonal close-packed structure in Fig. 3.33 is 3.633. The number of nearest-neighbor atoms is 12 for hcp structures. Table 3.4 shows the *c/a* parameter for different hexagonal crystals.

3.9.6 Wurtzite Structure

A few III–V and several II–VI semiconductor compounds have the wurtzite structure shown in Fig. 3.34.

This structure consists of two interpenetrating hexagonal close-packed lattices, each with different atoms, ideally displaced from each other by $3/8c$ along the z-axis. There is no inversion symmetry in this crystal, and polarity effects are observed along the z-axis. The Bravais lattice is hexagonal with a basis of four atoms, two of each kind. The point group of the wurtzite structure is C_{6v}.

3.9.7 Packing Factor

The packing factor is the maximum proportion of the available volume in a unit cell that can be filled with hard spheres. Let us illustrate this concept with a few examples.

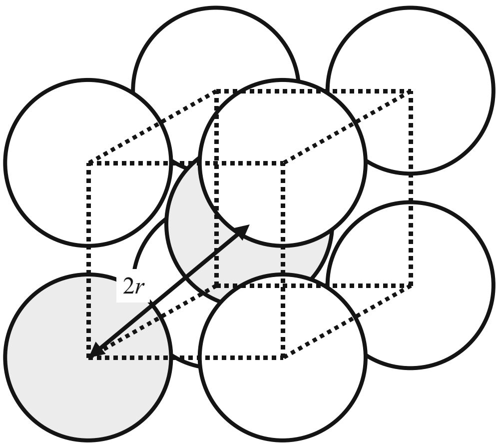
For a simple cubic lattice, the center-to-center distance between the nearest atoms is a. So the maximum radius of the atom is $a/2$. Since there is only one atom point per cubic unit cell in this case, the packing factor is $\frac{\frac{4}{3}\pi\left(\frac{a}{2}\right)^3}{a^3} = 0.52$.

The following two examples illustrate the determination of the packing factor for the other two cubic lattices.

Example

Q Determine the packing factor for a body-centered cubic lattice.

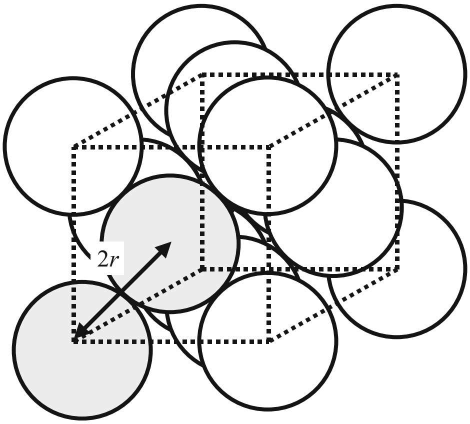
A Let us consider the bcc lattice shown in the figure below and an atom located at one corner of the cubic unit cell. Its nearest neighbor is an atom which is located at the center of the cubic unit cell and which is at a distance of $\frac{\sqrt{3}}{2}a$ where a is the side of the cube. The maximum radius r for the atoms is such that these two atoms touch and therefore $2r = \frac{\sqrt{3}}{2}a$. There are two atoms in a bcc cubic unit cell, so the maximum volume filled by the spheres is $2 \times \frac{4\pi}{3}\left(\frac{\sqrt{3}}{4}a\right)^3$. The packing factor is calculated by taking the ratio of the total sphere volume to that of the unit cell and yields $\frac{2\times\frac{4\pi}{3}\left(\frac{\sqrt{3}}{4}a\right)^3}{a^3} = \frac{\pi\sqrt{3}}{8} = 0.68$.



Example

Q Determine the packing factor for a face-centered cubic lattice.

A Let us consider the fcc lattice shown in the figure below and an atom located at one corner of the cubic unit cell. Its nearest neighbor is an atom which is located at the center of an adjacent face of the cubic unit cell and which is at a distance of $\frac{\sqrt{2}}{2}a$ where a is the side of the cube. The maximum radius r for the atoms is such that these two atoms touch and therefore $2r = \frac{\sqrt{2}}{2}a$. There are four atoms in a fcc cubic unit cell, so the maximum volume filled by the spheres is $4 \times \frac{4\pi}{3}\left(\frac{\sqrt{2}}{4}a\right)^3$. The packing factor is calculated by taking the ratio of the total sphere volume to that of the unit cell and yields: $\frac{4\times\frac{4}{3}\pi\left(\frac{\sqrt{2}}{4}a\right)^3}{a^3} = 0.7405$.



The diamond structure has the face-centered cubic structure with a basis of two identical atoms. The packing factor of diamond structure is only 46 percent of that in the fcc structure, so diamond structure is relatively empty (see Problems).

3.10 The Reciprocal Lattice

When we have a periodic system, one lattice point is equivalent to another lattice point, so we expect a simple relation to exist between physical quantities at these respective lattice points. Consider, for example, the local density of charge $\rho(\vec{r})$. We should expect this quantity to have the same periodicity as the lattice. But it is mathematically known that any periodic function can be expanded into a Fourier series. In a crystal lattice, all physical quantities have the periodicity of the lattice, in all directions. Let us consider the above physical quantity $\rho(\vec{r})$. From now, we will use a three-dimensional formalism. This function is periodic and can be expanded into a Fourier series:

$$\rho(\vec{r}) = \sum_{\vec{K}} \mathrm{P}(\vec{K}) \exp(i \vec{K} \vec{r}) \tag{3.6}$$

where the vector $\vec{K}$ is used to index the summation and the Fourier coefficients $\mathrm{P}(\vec{K})$. This vector $\vec{K}$ has the dimension of an inverse distance and, for a periodic function, can take on discrete values in a three-dimensional sum. Let us now express that the function $\rho(\vec{r})$ is periodic by calculating its value after displacement by a lattice vector $\vec{R}$:

$$\rho(\vec{r}) = \rho(\vec{r} + \vec{R}) = \sum_{\vec{K}} \mathrm{P}(\vec{K}) \exp\left[i \vec{K} \cdot (\vec{r} + \vec{R})\right] \tag{3.7}$$

which becomes

$$\sum_{\vec{K}} \mathrm{P}(\vec{K}) \exp(i \vec{K} \cdot \vec{r}) = \sum_{\vec{K}} \mathrm{P}(\vec{K}) \exp\left[i \vec{K} \cdot (\vec{r} + \vec{R})\right] \tag{3.8}$$

has to be satisfied for any given function which is periodic with the periodicity of the lattice. This can be satisfied if and only if

$$\exp\left[i \vec{K} \cdot (\vec{r} + \vec{R})\right] = \exp(i \vec{K} \cdot \vec{r})$$

or

$$\exp(i \vec{K} \cdot \vec{R}) = 1 \tag{3.9}$$

for any lattice vector Eq. (3.9) is the major relation which allows us to introduce the so-called reciprocal lattice which is spanned by the vectors $\vec{K}$. What follows next is a pure mathematical consequence of Eq. (3.9) which is equivalent to

$$\vec{K} \cdot \vec{R} = 2\pi m \tag{3.10}$$

where $m = 0, \pm 1, \pm 2, \ldots$ is an integer. Using the expression for $\vec{R}$ from Eq. (3.1) of Chap. 3, we obtain

$$(\vec{K} \cdot \vec{a}) n_1 + (\vec{K} \cdot \vec{b}) n_2 + (\vec{K} \cdot \vec{c}) n_3 = 2\pi m \tag{3.11}$$

where n_1, n_2, and n_3 are arbitrary integers which come from the choice of the vector $\vec{R}$. Because the sum of three terms is an integer if and only if each term itself is integer leads us to

$$\begin{cases} \vec{K} \cdot \vec{a} = 2\pi h_1 \\ \vec{K} \cdot \vec{b} = 2\pi h_2 \\ \vec{K} \cdot \vec{c} = 2\pi h_3 \end{cases} \text{with } h_{1,2,3} = 0; \pm 1; \pm 2, \ldots \tag{3.12}$$

Here, $h_{1,\,2,\,3}$ is not related to Planck's constant.

Let us now define three basis vectors ($\vec{A}$, $\vec{B}$, $\vec{C}$) in order to express $\vec{K}$ in the same way as we did it for real lattice vectors in Eq. (3.12) of Chap. 3. These basis vectors define what we call the reciprocal lattice. Any reciprocal lattice vector $\vec{K}$ can thus be represented as

$$\vec{K} = h_1 \vec{A} + h_2 \vec{B} + h_3 \vec{C}; \tag{3.13}$$

From (3.12) and (3.11), we have

$$\begin{cases} (\vec{A} \cdot \vec{a})h_1 + (\vec{B} \cdot \vec{a})h_2 + (\vec{C} \cdot \vec{a})h_3 = 2\pi h_1 \\ (\vec{A} \cdot \vec{b})h_1 + (\vec{B} \cdot \vec{b})h_2 + (\vec{C} \cdot \vec{b})h_3 = 2\pi h_2 \\ (\vec{A} \cdot \vec{c})h_1 + (\vec{B} \cdot \vec{c})h_2 + (\vec{C} \cdot \vec{c})h_3 = 2\pi h_3 \end{cases} \tag{3.14}$$

Equation (3.14) can be satisfied only when

$$\begin{cases} \vec{A} \cdot \vec{a} = \vec{B} \cdot \vec{b} = \vec{C} \cdot \vec{c} = 2\pi \\ \text{and} \\ \vec{A} \cdot \vec{b} = \vec{A} \cdot \vec{c} = 0 \\ \vec{B} \cdot \vec{a} = \vec{B} \cdot \vec{c} = 0 \\ \vec{C} \cdot \vec{b} = \vec{C} \cdot \vec{a} = 0 \end{cases} \tag{3.15}$$

Equation (3.15) defines the relation between the direct ($\vec{a}$, $\vec{b}$, $\vec{c}$) and reciprocal ($\vec{A}$, $\vec{B}$, $\vec{C}$) basis lattice vectors and gives the means to construct ($\vec{A}$, $\vec{B}$, $\vec{C}$) from ($\vec{a}$, $\vec{b}$, $\vec{c}$):

$$\begin{cases} \vec{A} = 2\pi \dfrac{\vec{b} \times \vec{c}}{\vec{a} \cdot \left(\vec{b} \times \vec{c}\right)} \\ \vec{B} = 2\pi \dfrac{\vec{c} \times \vec{a}}{\vec{a} \cdot \left(\vec{b} \times \vec{c}\right)} \\ \vec{C} = 2\pi \dfrac{\vec{a} \times \vec{b}}{\vec{a} \cdot \left(\vec{b} \times \vec{c}\right)} \end{cases} \tag{3.16}$$

These relations are a natural consequence of vector algebra in three dimensions. The volumes that these basis vectors define in the real and reciprocal lattices satisfy the relation (see Problems):

$$\vec{A} \cdot \left(\vec{B} \times \vec{C}\right) = \frac{8\pi^3}{\vec{a} \cdot \left(\vec{b} \times \vec{c}\right)} \tag{3.17}$$

We note that the vectors of reciprocal space have the same dimensions as the wavenumbers and momenta of electromagnetic waves. We also note the direct lattice is the reciprocal of its own reciprocal lattice. The concept of reciprocal or momentum space turns out to be extremely important for the classification of electron states in a crystal in quantum theory.

3.11 The Brillouin Zone

In the reciprocal lattice, we can construct unit cells as we did for the real lattice earlier in this chapter. The construction of the Wigner-Seitz cell in the reciprocal lattice follows the same rules as in the real lattice and gives the smallest unit cell in k-space called the "first Brillouin zone" and shown in Fig. 3.10. Draw the perpendicular bisector planes of the translation vectors from the chosen center to the nearest equivalent sites in the reciprocal lattice, and you have formed the first Brillouin zone.

3.12 Summary

In this chapter, the structure of crystals has been described. The concepts of Bravais lattice, crystal systems, unit cell, point groups, space groups, Miller indices, and packing factor have been introduced. The symmetry properties of crystals have been discussed. The most common crystal structures for semiconductors have been described. We have also introduced the concept of the reciprocal lattice. We have shown that for every periodic lattice in real space $\vec{R}$, it is possible to construct a periodic reciprocal lattice in $\vec{K}$ space. The reciprocal lattice is the lattice in so-called momentum space. The Wigner Seitz cell of the reciprocal lattice is called the first Brillouin zone.

Problems

1. Figure 3.6 illustrates the definition of the angles and unit cell dimensions of the crystalline material. If a unit cell has a characteristic of $a = b = c$ and $\alpha = \beta = \gamma = 90°$, it forms a cubic crystal system, which is the case of Si and GaAs.
   (a) How many Bravais lattices are classified in the cubic system?
   (b) Draw simple three-dimensional unit cells for each Bravais lattice in the cubic system.
   (c) How many lattice points are contained in the unit cell for each Bravais lattice in the cubic system?
2. Draw the four Bravais lattices in orthorhombic lattice system.
3. Show that the C_5 group is not a crystal point group. In other words, show that, in crystallography, a rotation about an axis and through an angle $\theta = \frac{2\pi}{5}$ cannot be a crystal symmetry operation.
4. Determine if the plane (111) is parallel to the following directions: [100], $\left[\bar{2}11\right]$, and $\left[\bar{1}\bar{1}0\right]$.
5. For cesium chloride, take the fundamental lattice vectors to be $\vec{a} = a\,\vec{x}$, $\vec{b} = a\,\vec{y}$, and $\vec{c} = a\left(\vec{x} + \vec{y} + \vec{z}\right)$. Describe the parallelepiped unit cell and find the cell volume.
6. GaAs is a typical semiconductor compound that has the zinc blende structure.
   (a) Draw a cubic unit cell for the zinc blende structure showing the positions of Ga and As atoms.
   (b) Make a drawing showing the in-plane crystallographic directions and the positions of the atoms for the (111) lattice plane.
   (c) Repeat for the (100) plane.
   (d) Calculate the surface density of atoms in (100) plane.
7. (a) What are the interplanar spacings d for the (100), (110), and (111) planes of Al ($a = 4.05$ Å)?
   (b) What are the Miller indices of a plane that intercepts the x-axis at a, the y-axis at $2a$, and the z-axis at $2a$?
8. Show that the c/a ratio for an ideal hexagonal close-packed structure is $(8/3)^{1/2} = 1.633$. 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.
9. Show that the packing factor in a hexagonal close-packed structure is 0.74.
10. Show that the packing factor for the diamond structure is 46% of that in the fcc structure.

11. Let $(\vec{a}, \vec{b}, \vec{c})$ be a basis lattice vectors for a direct lattice and $(\vec{A}, \vec{B}, \vec{C})$ be the basis lattice vectors for the reciprocal lattice defined by Eq. (3.16). Prove that the volume defined by these vectors is given by $\vec{A}\cdot\left(\vec{B}\times\vec{C}\right) = \frac{8\pi^3}{\vec{a}\cdot\left(\vec{b}\times\vec{c}\right)}$.

Further Reading

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