Section 1: Crystal Structure

A solid is said to be a crystal if atoms are arranged in such a way that their positions are *exactly periodic*. This concept is illustrated in Fig.1 using a two-dimensional (2D) structure.

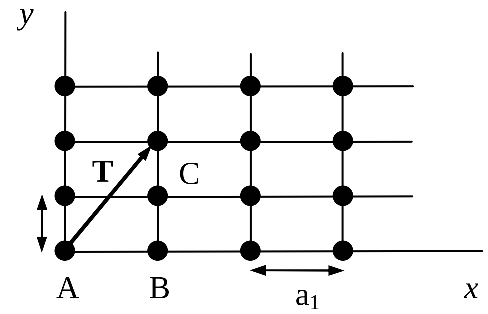


Fig.1

A perfect crystal maintains this periodicity in both the *x* and *y* directions from -∞ to +∞. As follows from this periodicity, the atoms A, B, C, etc. are *equivalent*. In other words, for an observer located at any of these atomic sites, the crystal appears exactly the same.

The same idea can be expressed by saying that a crystal possesses a *translational symmetry*. The translational symmetry means that if the crystal is translated by any vector joining two atoms, say **T** in Fig.1, the crystal appears exactly the same as it did before the translation. In other words the crystal remains *invariant* under any such translation.

The structure of all crystals can be described in terms of a *lattice*, with a group of atoms attached to every lattice point. For example, in the case of structure shown in Fig.1, if we replace each atom by a geometrical point located at the equilibrium position of that atom, we obtain a crystal lattice. The crystal lattice has the same geometrical properties as the crystal, but it is devoid of any physical contents.

There are two classes of lattices: the *Bravais* and the *non-Bravais*. In a Bravais lattice all lattice points are equivalent and hence by necessity all atoms in the crystal are of the same kind. On the other hand, in a non-Bravais lattice, some of the lattice points are non-equivalent.

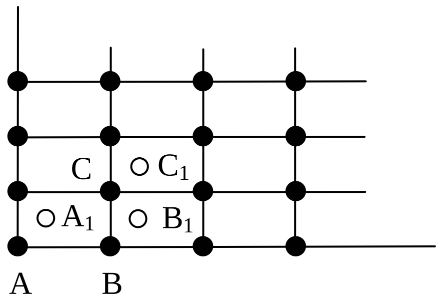


Fig.2

In Fig.2 the lattice sites A, B, C are equivalent to each other. Also the sites A_1, B_1, C_1, are equivalent among themselves. However, sites A and A_1 are not equivalent: the lattice is not invariant under translation AA_1.

Non-Bravais lattices are often referred to as a *lattice with a basis*. The basis is a set of atoms which is located near each site of a Bravais lattice. Thus, in Fig.2 the basis is represented by the two atoms A and A_1. In a general case crystal structure can be considered as

crystal structure = lattice + basis.

The lattice is defined by fundamental translation vectors. For example, the position vector of any lattice site of the two dimensional lattice in Fig.3 can be written as

$$\mathbf{T}=n_1\mathbf{a}_1+n_2\mathbf{a}_2\,, \qquad (1.1)$$

where $\mathbf{a}_1$ and $\mathbf{a}_2$ are the two vectors shown in Fig.3, and n_1,n_2 is a pair of integers whose values depend on the lattice site.

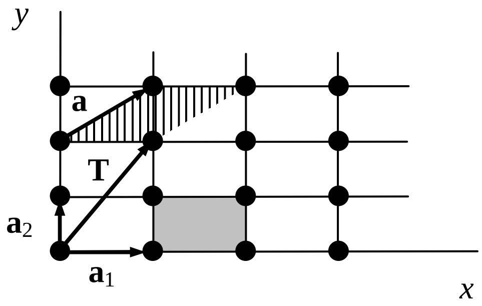


Fig.3

So, the two non-collinear vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ can be used to obtain the positions of all lattice points which are expressed by Eq.(1). The set of all vectors **T** expressed by this equation is called the *lattice vectors*. Therefore, the lattice has a translational symmetry under displacements specified by the lattice vectors **T**. In this sense the vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ can be called *the primitive translation vectors*.

The choice of the primitive translations vectors is not unique. One could equally well take the vectors $\mathbf{a}_1$ and $\mathbf{a} = \mathbf{a}_1+\mathbf{a}_2$ as primitive translation vectors (see Fig.3). This choice is usually dictated by convenience.

Unit cell. In the case of a rectangular two dimensional lattice the unit cell is the rectangle, whose sides are the vectors $\mathbf{a}_1$ and $\mathbf{a}_2$. If the unit cell is translated by all the lattice vectors expressed by Eq.(1), the area of the whole lattice is covered once and only once. A *primitive unit cell* is the unit cell with the smallest area which produces this coverage. In the two dimensional case the area of the unit cell is given by $S=|\mathbf{a}_1\times\mathbf{a}_2|$.

The choice of the unit cell is not unique. For example, the parallelogram formed by the vectors $\mathbf{a}_1$ and **a** in Fig.3 is also an acceptable unit cell. The choice is again dictated by convenience. The area of the unit cell based on vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ is the same as that based on vectors $\mathbf{a}_1$ and **a**.

Wigner-Seits unit cell. The primitive cell may be chosen as shown in Fig.4. (i) Draw lines to connect a given lattice point to all nearby lattice points. (ii) At the midpoint and normal to these lines, draw new lines (planes in 3D). The smallest volume enclosed is the Wigner-Seitz primitive cell. All the space of the crystal may be filled by these primitive cells, by translating the unit cell by the lattice vectors.

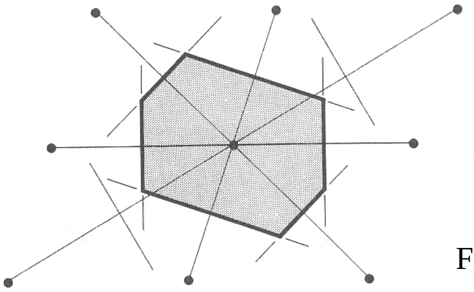


Fig.4

The unit cell can be *primitive* and *non-primitive* (or *conventional*). The unit cell discussed above is primitive. However, in some cases it is more convenient to deal with a unit cell which is larger, however, it exhibits the symmetry of the lattice more clearly.

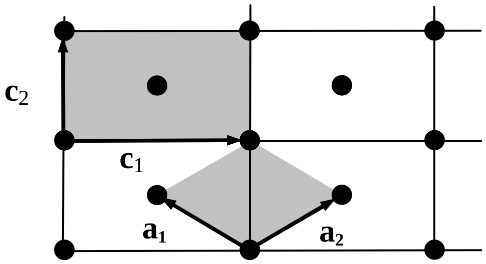


Fig.5

Vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ can be chosen as primitive translation vectors for the lattice shown in Fig.5. In this case the unit sell is parallelogram. However, the lattice can also be regarded as adjacent rectangles, where the vectors $\mathbf{c}_1$ and $\mathbf{c}_2$ can be considered as primitive translation vectors. The unit cell in this case is larger, however it exhibits the rectangular symmetry more clearly. In the first case we have just one atom in a unit cell, whereas in the second case we have a lattice with a basis. The basis consists of the two atoms: one atom is located in the corner of the unit cell and another atom in the center of the unit cell. The area of the conventional unit cell is larger by a factor of two than the area of the primitive unit cell.

Crystal lattices are classified according to their symmetry properties, such as inversion, reflection and rotation.

Inversion center. A cell has an inversion center if there is a point at which the cell remains invariant under transformation $\mathbf{r} \rightarrow -\mathbf{r}$. All the Bravais lattices are inversion symmetric. Non-Bravais lattices may or may not have an inversion center depending on the symmetry of the basis.

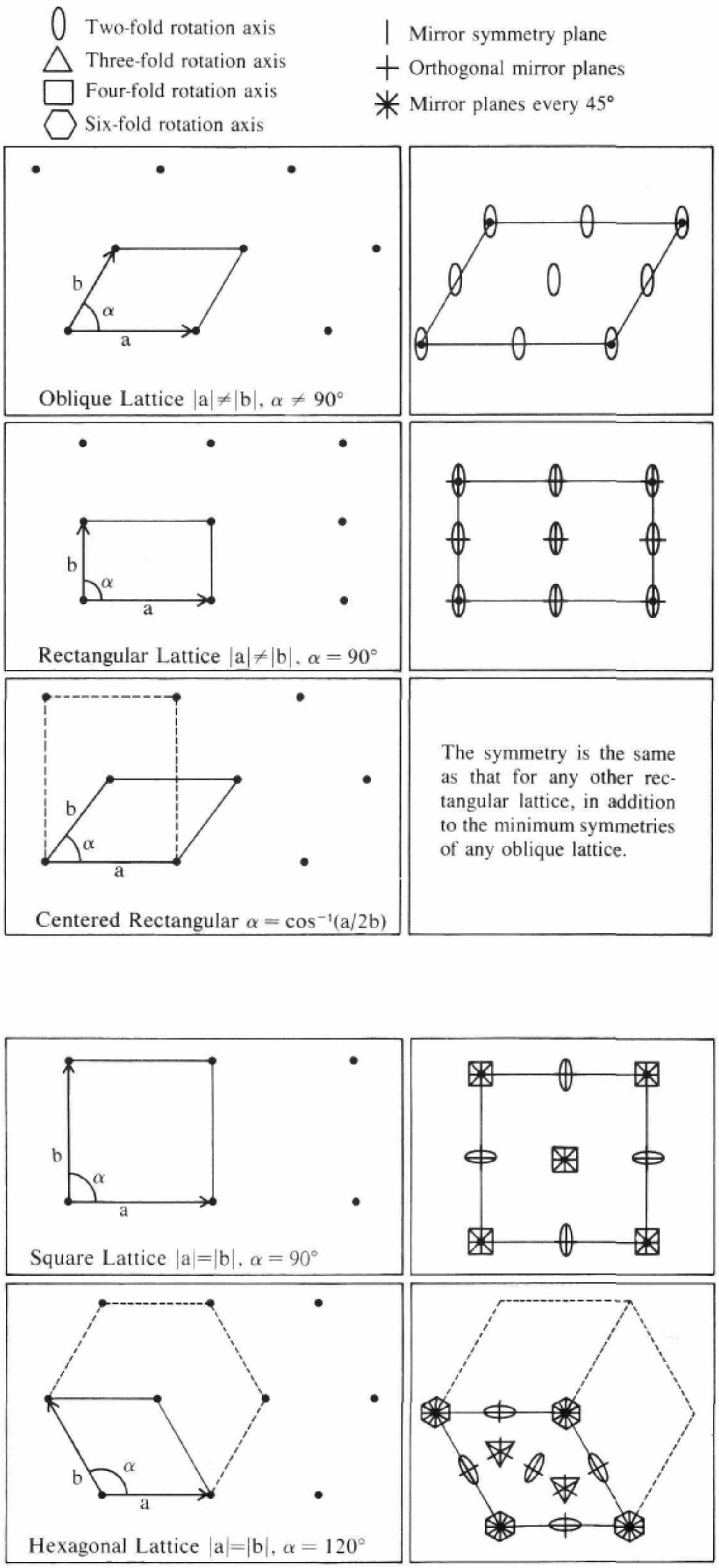
Reflection plane. A cell has a reflection plane if it remains invariant when a mirror reflection in this plane is performed.

Rotation axis. This is an axis such that, if the cell rotated around the axis trough some angle, the cell remains invariant. The axis is called *n*-fold if the angle of rotation is $2\pi/n$. Only 2-, 3-, 4-, and 6-fold axes are possible.

There are five Bravais lattice types in two dimensions shown in Fig.6. For each of them the rotation axes and/or mirror planes occur at the lattice points. However, there are other locations in the unit cell with comparable or lower degrees of symmetry with respect to rotation and reflection.

For non-Bravais lattices we have to take into account the symmetry of the basis which is referred as *point-group symmetry*. The point group symmetry includes all possible rotations, reflections and inversion, which leave the basis invariant. Point groups are denoted by a numerical and "*m*". The numerical indicates how many positions within the basis are equivalent by rotation symmetry. A single *m* shows that the basis has a mirror plane symmetry. (In two dimensions – it is mirror axis). E.g., 3*m* means that there are 3 equivalent sites within the unit cell and there is one mirror plane. In two dimensions there are 10 point groups.

When we combine the rotation symmetry of the point group with the transnational symmetries, we obtain a *space-group symmetry*.



The symmetry is the same as that for any other rectangular lattice, in addition to the minimum symmetries of any oblique lattice.

Fig.6

All the lattice properties we discussed for two dimensions can be extended to three dimensions. The lattice vectors are in this case

$$\mathbf{T}=n_1\mathbf{a}_1+n_2\mathbf{a}_2+n_3\mathbf{a}_3 \qquad (1.2)$$

where $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ are the primitive translation vectors, and (n_1,n_2,n_3) are a triplet of integers whose values depend on a particular lattice site. The unit cell in three dimensions is a parallelepiped, whose sides are the primitive translation vectors (see Fig.7). Here again the choice of the unit cell is not unique, although all primitive unit cells have equal volumes. The unit cell fills all space by the repetition of crystal translation operations. The volume of the unit cell represented by a parallelepiped with sides $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ is given by

$$V=|\mathbf{a}_1\cdot\mathbf{a}_2\times\mathbf{a}_3|. \qquad (1.3)$$

Also, it is sometimes more convenient to deal with non-primitive or conventional cells, which have additional lattice sites either inside the cell or on its surface.

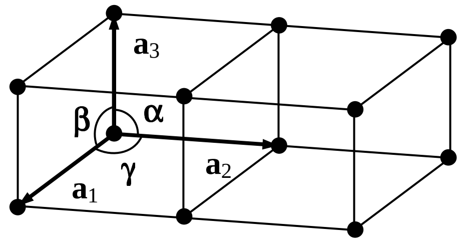


Fig.7

In three dimensions there are 14 different Bravais crystal lattices which belong to 7 crystal systems. These systems are triclinic, monoclinic, orthorhombic, tetragonal, cubic, hexagonal and trigonal. The crystal lattices are shown in Fig.8. In all the cases the unit cell represents a parallelepiped whose sides are $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$. The opposite angles are called α, β and γ. The relationship between the sides and the angles determines the crystal system. A simple lattice has sites only at the corners, a body-centered lattice has one additional point at the center of the cell, and a face-centered lattice has six additional points, one on each side. Note that in all the non-simple lattices the unit cells are non-primitive. The volume of the primitive unit cell is equal to the volume of the conventional unit cell divided by the number of sites.

Each of the 14 lattices has one or more types of symmetry properties with respect to reflection and rotation.

Reflection: The triclinic structure has no reflection plane, the monoclinic has one plane midway between and parallel to the basis plane, and so forth. The cubic cell has nine reflection planes: three parallel to the faces, and six other, each of which passes through two opposite edges.

Rotation: The triclinic structure has no axis of rotation (do not take into account 1-fold axis), the monoclinic has a 2-fold axis normal to the base. The cubic cell has three 4-fold axis normal to the faces and four 3-fold axis, each passing through two opposite corners.

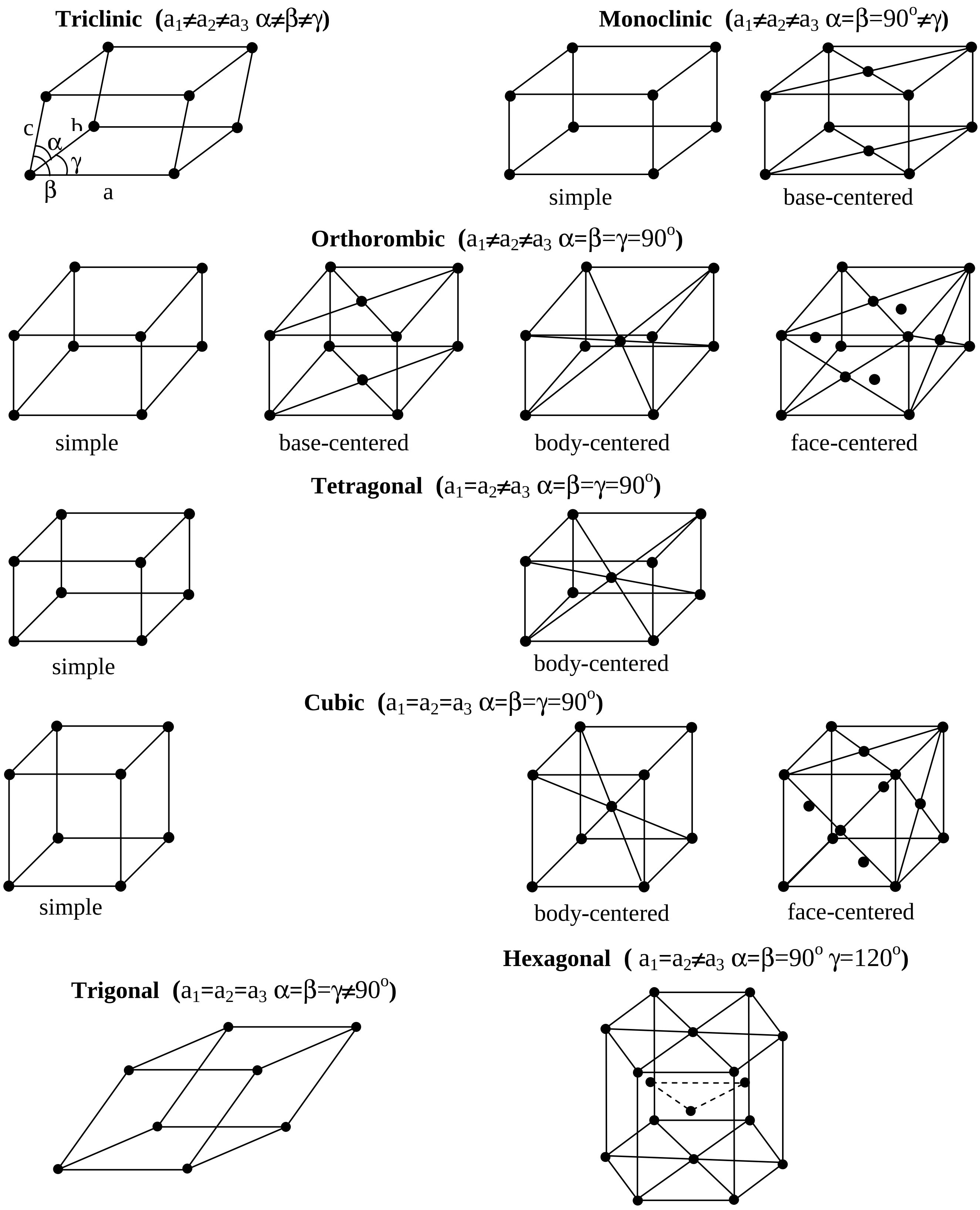
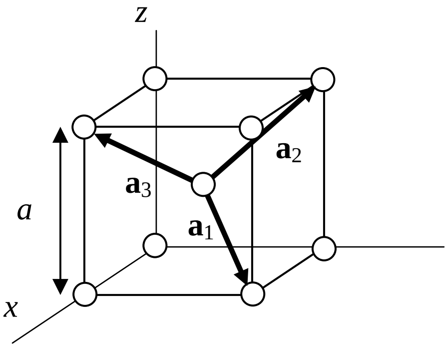
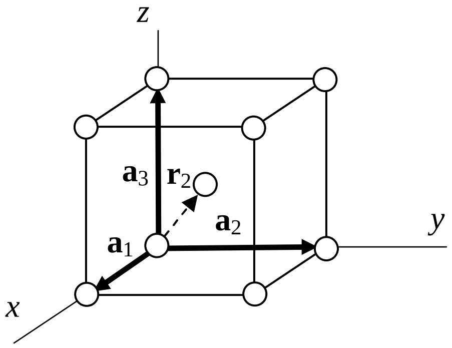

Triclinic ($a_1 \neq a_2 \neq a_3$ $\alpha \neq \beta \neq \gamma$)
c
b
α
γ
β
a
Monoclinic ($a_1 \neq a_2 \neq a_3$ $\alpha = \beta = 90^o \neq \gamma$)
simple
base-centered
Orthorombic ($a_1 \neq a_2 \neq a_3$ $\alpha = \beta = \gamma = 90^o$)
simple
base-centered
body-centered
face-centered
Tetragonal ($a_1 = a_2 \neq a_3$ $\alpha = \beta = \gamma = 90^o$)
simple
body-centered
Cubic ($a_1 = a_2 = a_3$ $\alpha = \beta = \gamma = 90^o$)
simple
body-centered
face-centered
Hexagonal ($a_1 = a_2 \neq a_3$ $\alpha = \beta = 90^o$ $\gamma = 120^o$)
Trigonal ($a_1 = a_2 = a_3$ $\alpha = \beta = \gamma \neq 90^o$)

Fig.8

Most common crystal structures

Body-centered cubic (bcc) lattice:



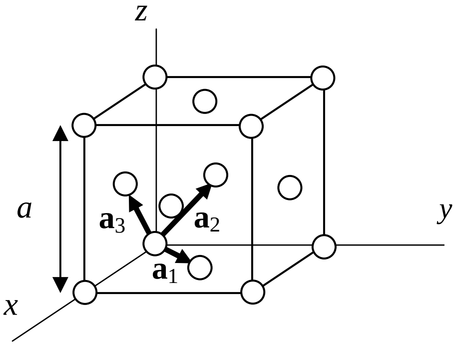


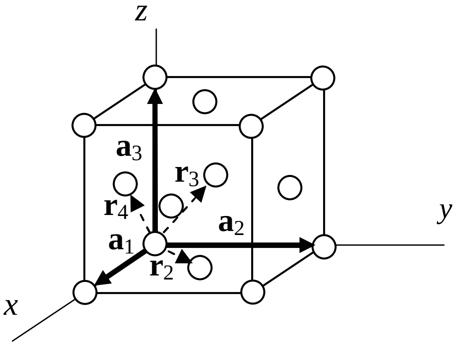
Primitive translation vectors of the bcc lattice (in units of lattice parameter a) are $\mathbf{a}_1$ = ½½-½; $\mathbf{a}_2$ = -½½½; $\mathbf{a}_3$ = ½-½½. The primitive cell is the rhombohedron. The packing ratio is 0.68, defined as the maximum volume which can be filled by touching hard spheres in atomic positions. Each atom has 8 nearest neighbors.

The conventional unit cell is a cube based on vectors $\mathbf{a}_1$ = 001; $\mathbf{a}_2$ = 010; $\mathbf{a}_3$ = 001. It is twice big compared to the primitive unit cell and has two atoms in it with coordinates $\mathbf{r}_1$ = 000 and $\mathbf{r}_2$ = ½½½.

The bcc lattice have alkali metals such as Na, Li, K, Rb, Cs, magnetic metals such as Cr and Fe, and and refractory metals such as Nb, W, Mo ,Ta.

Face-centered cubic (fcc) lattice:



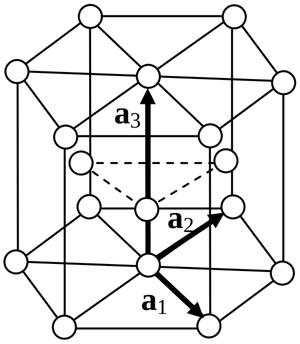


Primitive translation vectors of the bcc lattice (in units of lattice parameter a) are $\mathbf{a}_1$ = ½½0; $\mathbf{a}_2$ = 0½½; $\mathbf{a}_3$ = ½ 0½. The primitive cell is the rhombohedron. The packing ratio is 0.74. Each atom has 12 nearest neighbors.

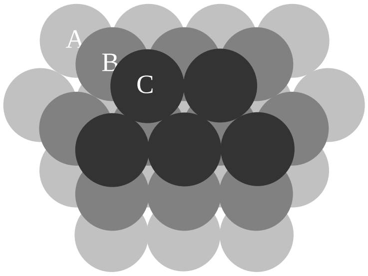
The conventional unit cell is a cube based on vectors $\mathbf{a}_1$ = 001; $\mathbf{a}_2$ = 010; $\mathbf{a}_3$ = 001. It is 4 times bigger than the primitive unit cell and has 4 atoms in it with coordinates $\mathbf{r}_1$ = 000; $\mathbf{r}_2$ = ½½0; $\mathbf{r}_3$ = 0½½; $\mathbf{r}_4$ = ½0½.

The fcc lattice have noble metals such as Cu, Ag, Au, common metals such as Al, Pb, Ni and inert gas solids such as Ne, Ar, Kr, Xe.

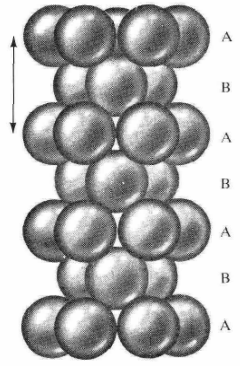
Hexagonal closed-packed (hcp) lattice:



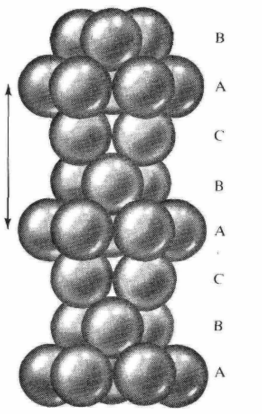
The hcp structure has $a_1=a_2\neq a_3$, $\alpha=\beta=90^o$ and $\gamma=120^o$ with a basis of two atoms, one at 000 and the other at $\frac{2}{3}\frac{1}{3}\frac{1}{2}$. Along with the fcc structure, the hcp structure maximizes the packing ratio, making it 0.74.



close-packed structure (fcc)



hcc structure

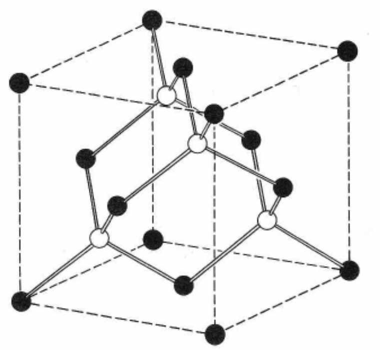


fcc structure

A closed-packed structure is created by placing a layer of spheres B on top of identical close-packed layer of spheres A. 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 hcp. If the third layer goes in over *C* the sequence is ABCABCABC. . . and the structure is fcc.

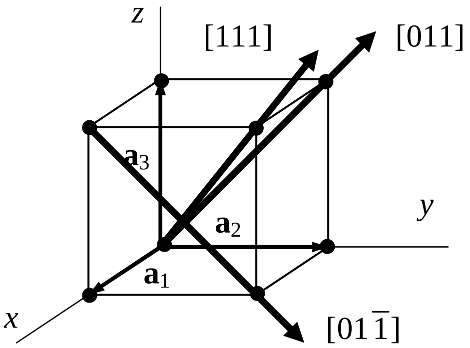
In perfect hcp structure the ratio of the height of the cell to the nearest neighbor spacing is $(8/3)^{1/2}$. In practice the (a_3/a_1) ratio is larger than 1.633 for most hexagonal crystals. Examples of nominally hcp crystals include the elements from Column II of the Periodic Table: Be, Mg, Zn, and Cd. Hcp is also the stable structure for several transition elements, such as Ti and Co.

Diamond structure is adopted by solids with four symmetrically placed covalent bonds. This is the situation in silicon, germanium, and grey tin, as well as in diamond. Diamond has the translational symmetry of fcc lattice with a basis of two atoms, one at 000 and the other at ¼¼¼. Diamond structure represents two inter-penetrating fcc sublattices displaced from each other by one quarter of the cube diagonal distance.

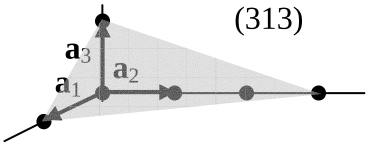


Index system for crystal directions and planes

Crystal directions. Any lattice vector can be written as that given by Eq.(1.2). The direction is then specified by the three integers $[n_1n_2n_3]$. If the numbers $n_1n_2n_3$ have a common factor, this factor is removed. For example, [111] is used rather than [222], or [100], rather than [400]. When we speak about directions, we mean a hole set of parallel lines, which are equivalent due to transnational symmetry. Opposite orientation is denoted by the negative sign over a number. For example:



Crystal planes. The orientation of a plane in a lattice is specified by *Miller indices*. They are defined as follows. We find intercept of the plane with the axes along the primitive translation vectors $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$. Let's these intercepts be *x*, *y*, and *z*, so that *x* is fractional multiple of a_1, *y* is a fractional multiple of a_2 and *z* is a fractional multiple of a_3. Therefore we can measure *x*, *y*, and *z* in units a_1, a_2 and a_3 respectively. We have then a triplet of integers (*x y z*). Then we invert it (1/*x* 1/*y* 1/*z*) and reduce this set to a similar one having the smallest integers by multiplying by a common factor. This set is called Miller indices of the plane (*hkl*). For example, if the plane intercepts *x*, *y*, and *z* in points 1, 3, and 1, the index of this plane will be (313).



The Miller indices specify not just one plane but an infinite set of equivalent planes. Note that for cubic crystals the direction [hkl] is perpendicular to a plane (hkl) having the same indices, but this is not generally true for other crystal systems. Examples of the planes in a cubic system: