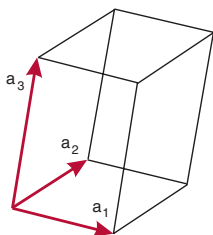


Primitive Cell

A substance is considered to be in a crystalline state (known as a **crystal**) if its constituent atoms are arranged in a regular and repetitive pattern.

Crystals can be described by an object that, when repeated, generates the entire crystal. Such an object can be considered as a “building block” called a **unit cell**. The unit cell is spanned by three independent vectors \mathbf{a}_1 , \mathbf{a}_2 , and \mathbf{a}_3 , which may or may not lie along the Cartesian coordinate axes. It contains only one lattice point, and its volume is



$$\Omega = (\mathbf{a}_1 \times \mathbf{a}_2) \cdot \mathbf{a}_3$$

Its vertices define the lattice points. Each unit cell has the same shape, volume, and atomic arrangements. The choice of unit cell is not unique, and there is an infinite number of possible ways to choose a unit cell. The smallest possible unit cell is called the **primitive cell**. The vectors that define a primitive cell are called **primitive lattice vectors**.

The symmetry of a crystal is determined by the arrangement of atoms in its unit cell. A simple cubic unit cell is the simplest 3D case. Each of its eight corners contains identical atoms. More-complicated cases can have atoms in the center of the faces or at the center of the cube, known as a face-centered or body-centered cubic unit cell, respectively. They are important structures because many metals, ionic solids, and intermetallic compounds crystallize in such structures. Experimental techniques for studying crystal structures include

- x-ray diffraction structural analysis,
- neutron diffraction, and
- electron diffraction.

Bravais Lattice

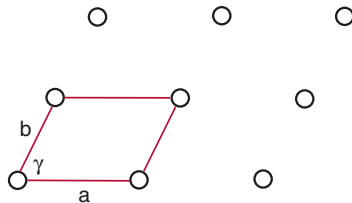
An ideal crystal, i.e., without defects or imperfections, consists of a regular arrangement of atoms. A **Bravais lattice (BL)** is used to characterize such systems. It is a mathematical set of points that are equivalent to each other. The various symmetry operations (see “Elements of Symmetry”) possible for a 3D set of points result in 14 different BLs. Each lattice represents a set of points in a space that forms a periodic structure. Each point has exactly the same environment. The **lattice points** are specified by a **lattice vector \mathbf{R}** as

$$\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$$

where n_1 , n_2 , and n_3 are integers, and \mathbf{a}_1 , \mathbf{a}_2 , and \mathbf{a}_3 are three independent vectors.

Representative unit cells of the 14 BLs are shown on page 4. An important role is played by a face-centered cubic lattice, which is a structure that appears in many semiconductors.

It is often important to know the arrangement of neighboring atoms, especially the **nearest neighbors (NNs)**. The number of NNs of an atom is known as the **coordination number**. A BL can also be introduced in two dimensions; a 2D lattice can be specified by vectors \mathbf{a} and \mathbf{b} and the angle γ (of specific value) between them. Other 2D lattices are square, rectangular, centred rectangular, and hexagonal. Symmetry operations, like those for 3D structures, can be used to describe 2D structures.



For crystals with many atoms, a building block of atoms, called the basis, is associated with each lattice point. Together, they create the crystal structure.

Elements of Symmetry

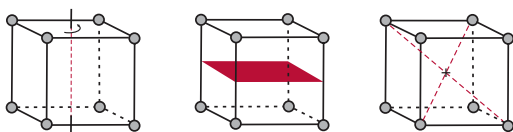
An ideal crystal possesses a certain type of **symmetry**. Crystal symmetry is defined by a group of operations that leave the crystal invariant. Operations that are applied through some fixed points within a unit cell are called **point group operations**.

Operations (coordinate transformations) include reflections, rotations, inversions, and translations by a vector of a fraction of a lattice vector. If the translations are followed by the point group operations, then these operations define a space group. Typically, a unit cell is expected to be invariant under certain transformations, which defines the symmetries possessed by a crystal. In crystals, rotations are only allowed for particular angles $\theta_n = 2\pi/n$, where $n = 2, 3, 4, 6$, consistent with translations of lattice vectors. Such an axis of symmetry is of the n^{th} -fold axis and is denoted as C_n . A cube has three types of symmetrical axes:

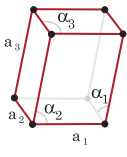
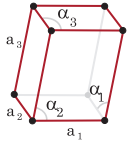
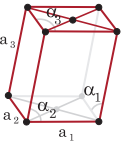
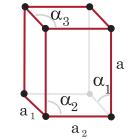
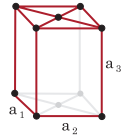
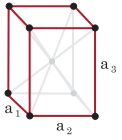
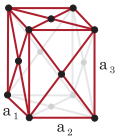
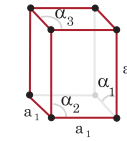
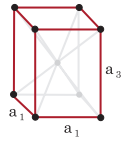
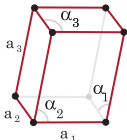
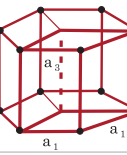
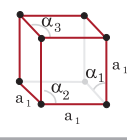
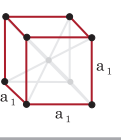
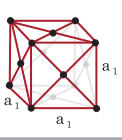
- three C_4 axes that pass through the centers of opposite faces,
- four C_3 axes that are along diagonals, and
- six C_2 axes that pass through the midpoints of opposite edges.

Each axis has counterclockwise and clockwise rotations. The same rule applies to other rotational axes.

Some symmetry operations for the simple cubic structure are illustrated below. The left image shows rotation through an axis, the middle image shows mirror reflection with respect to a plane, and the right image shows inversion through a point. All of these operations pass through the center of the cube. There are a total of 32 point symmetry groups that describe various properties of solid state systems.



Summary of Bravais Lattices

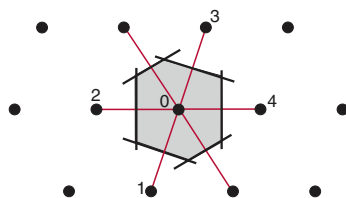
	Simple	Base-centered	Body-centered	Face-centered
Triclinic				
Monoclinic				
Orthorhombic				
Tetragonal				
Rhombohedral				
Hexagonal				
Cubic				

Wigner–Seitz Cell

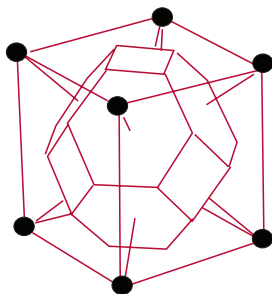
A **Wigner–Seitz (WS) cell** is a special primitive cell that contains one lattice point. The WS cell is defined for a general lattice as the smallest polyhedron bounded by planes that are the perpendicular bisectors joining one lattice point to the others. The WS cell has the smallest possible volume (3D) and area (2D).

The WS cell in the reciprocal lattice defines the first BZ and has the full symmetry of the BL. It is constructed around an arbitrary lattice point, and when translated over all lattice points, it will fill the space of the entire crystal without overlapping.

It is difficult to illustrate the construction of a WS cell in 3D, so the image here depicts the construction of a WS cell in 2D real space.



- Select an arbitrary atom 0.
- Determine the NN atoms of the same species as the chosen atom.
- Draw lines from the atom 0 to all NNs, e.g., lines from atom 0 to all atoms 1, 2, 3, 4.
- Draw lines (planes, in 3D) passing through the middle of the lines. The cell enclosed by those lines (planes) is the WS primitive cell.

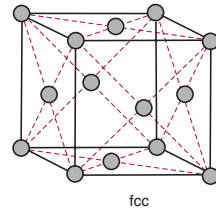
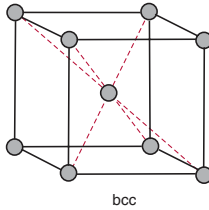


The 3D WS cell for the body-centered cubic lattice shown here is a truncated octahedron with volume $\frac{1}{2}a^3$. The cube around it is a conventional body-centered cubic cell with a lattice point on each vertex and at its center.

Body- and Face-Centered Cubic Structures

Body-centered cubic (bcc) and **face-centered cubic (fcc)** structures are important lattices because they appear in many solids, e.g., Ar, Ag, and Ce (fcc) and Ba, Cr, Fe, K, and Li (bcc). Both structures are modified from the simple cubic system and are shown here with the locations of the atoms.

The bcc structure has eight atoms at the corners and one atom at the body center. Assume that



\hat{a}_x , \hat{a}_y , \hat{a}_z are primitive vectors of the simple cubic lattice, where \hat{x} , \hat{y} , \hat{z} are orthogonal unit vectors. They also define the conventional cell of the bcc structure, which is also determined by the following vectors for this cell (not shown here):

$$\mathbf{a}_1 = \hat{a}_x, \mathbf{a}_2 = \hat{a}_y, \mathbf{a}_3 = \frac{\mathbf{a}}{2}(\hat{x} + \hat{y} + \hat{z})$$

The bcc structure can also be described by the more symmetric set of vectors

$$\mathbf{a}_1 = \frac{\mathbf{a}}{2}(\hat{y} + \hat{z} - \hat{x}), \mathbf{a}_2 = \frac{\mathbf{a}}{2}(\hat{x} + \hat{z} - \hat{y}), \mathbf{a}_3 = \frac{\mathbf{a}}{2}(\hat{x} + \hat{y} - \hat{z})$$

In this structure, the **coordination number**, i.e., the number of NNs, is 8. The bcc structure shown here belongs to the body-centered BLs.

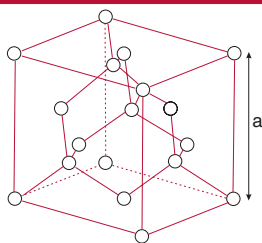
Similarly, a symmetric set of primitive vectors for a fcc lattice is

$$\mathbf{a}_1 = \frac{\mathbf{a}}{2}(\hat{y} + \hat{z}), \mathbf{a}_2 = \frac{\mathbf{a}}{2}(\hat{x} + \hat{z}), \mathbf{a}_3 = \frac{\mathbf{a}}{2}(\hat{x} + \hat{y})$$

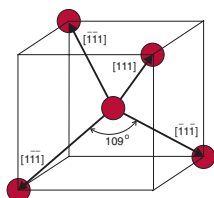
There are only two fcc lattices among the 14 BLs—one in the cubic system, and another in the orthorhombic system.

Diamond Structure

In a **diamond structure** in the conventional fcc lattice (shown here with the locations of atoms and the bonds (lines) between them), all atomic sites are occupied by carbon atoms. Semiconductors such as diamond (C), silicon (Si), germanium (Ge), and grey tin (α -Sn) crystallize in this structure.



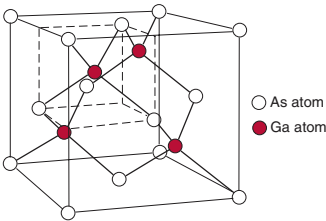
The structure is a combination of two identical interpenetrating fcc lattices. One of the sublattices is shifted along the body diagonal of the cubic cell by one quarter of the length of the diagonal. The diamond structure is thus fcc with a basis containing two identical atoms.



A simple method for constructing a diamond lattice considers it as a fcc structure with an extra atom placed at $\frac{1}{4}\mathbf{a}_1 + \frac{1}{4}\mathbf{a}_2 + \frac{1}{4}\mathbf{a}_3$ from each of the fcc atoms. The basic element of the structure is a tetrahedron where a C atom is at the center, and its four NNs are at the corners of the cube (or vice versa). Each atom forms four bonds with its NNs. Atoms in diamond-type crystals form covalent bonding. The bonding energy is associated with the shared valence electrons between atoms and depends on the relative orientation of atoms.

The atomic arrangement in the diamond structure helps explain its mechanical, chemical, and metallurgical properties. These semiconductor crystals can be cleaved along certain atomic planes to produce excellent planar surfaces, e.g., diamonds used in jewelry. Such surfaces are used as Fabry–Pérot reflectors in semiconductor lasers. Chemical reactions performed with such crystals, such as etching, often occur preferentially in certain directions.

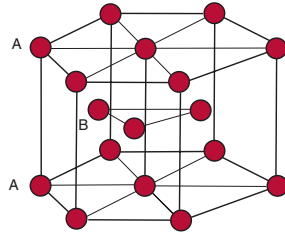
Zincblende and Hexagonal Structures



A **zincblende structure** has the form of a diamond except that the two sublattices are occupied by different types of atoms, e.g., As and Ga, as shown here. It is a fcc structure with a two-atom basis. The

structure is typical for semiconductors such as GaAs, ZnS, ZnSe, SiC, and GaP. For example, in ZnS, the Zn atoms occupy positions $(0, 0, 0)$, $(0, \frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2}, 0, \frac{1}{2})$, $(\frac{1}{2}, \frac{1}{2}, 0)$, and S atoms occupy positions $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, $(\frac{1}{4}, \frac{3}{4}, \frac{3}{4})$ and $(\frac{3}{4}, \frac{1}{4}, \frac{3}{4})$, $(\frac{3}{4}, \frac{3}{4}, \frac{1}{4})$. Each atom has four equally distant neighbors of the opposite type located at the corners of a regular tetrahedron. There are four molecules of ZnS per conventional cell. In this compound, the presence of two different kinds of atoms means that the system does not have inversion symmetry.

Another important structure is the **hexagonal close-packed (hcp) structure**. All atoms in the A-plane have an identical environment and can be taken as lattice points. Atoms that form the B-plane “feel” different environmentally and do not lie on lattice points. The unit cell contains a basis of an A atom



at $(0, 0, 0)$ and a B atom at $(\frac{2}{3}, \frac{1}{3}, \frac{1}{2})$. There are two atoms in each primitive unit cell. The close-packed A-planes form two horizontal planes, and the B-planes are halfway between. The fcc structure has a hexagonal packing in the direction along $[111]$, the cube diagonal. However, it is a close packing with three layers ABC instead of two, as in the hcp (e.g., Ti, Mg, Cd, Zn, He).