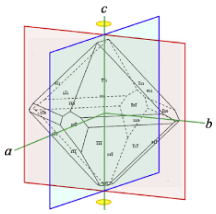
Chapter 1
Crystal Structures



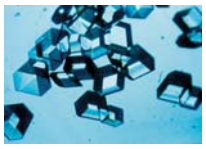
Lee Chow
ENG1 386

Outline

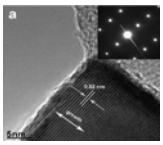
1. **Periodic arrays of atoms**
2. **Fundamental types of lattices**
3. **Position and orientation of planes in crystals**

Quartz

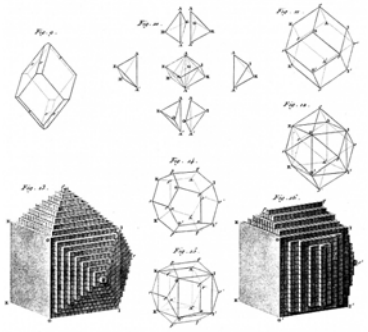
Calcium Carbonate



Insulin crystals grown in space



ZnO crystal grown at UCF



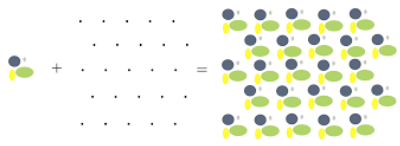
Abbé Haüy, an early French philosopher of geometry, was among the first to investigate the crystalline structure in a scientific way – and produced his masterpiece the Traité de Cristallograhie in 1822.

Periodic arrays of atoms

A crystal is composed of infinite repetition of identical structure.

Lattice ⇒ **Infinite repetition of identical structure**

Basis ⇒ **Pattern in each identical structure**



Basis Lattice Crystal Structure

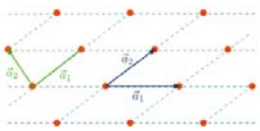
Because of the repetition, the crystal structure looks the same from $\vec{r}$ or $\vec{r'}$, when

$$\vec{r'} = \vec{r} + u_1\vec{a} + u_2\vec{b} + u_3\vec{c} = \vec{r} + \vec{T}$$

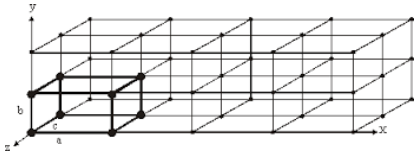
Where $\vec{T}$ is the translation vector, u_1, u_2, and u_3 are integers, and $\vec{a}$, $\vec{b}$, and $\vec{c}$ are primitive vectors. The volume defined by the primitive vectors is called a primitive cell.

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

Two dimensional example of primitive cell. The way to define a primitive cell is not unique.

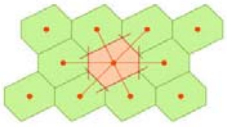


A primitive cell in 3D



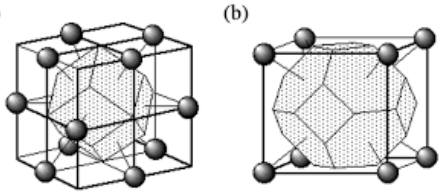
Inside a primitive cell there is only one basis. There are many ways to construct a primitive cell.

A Wigner-Seitz cell is a primitive cell by connecting a lattice point to all its neighbors, then draw normal lines at midpoint, Wigner-Seitz cell.



Wigner-Seitz cells in 3D, (a) fcc lattice, (b) bcc lattice.

(a) (b)



rhombic dodecahedron truncated octahedron

Fundamental types of lattices

There are operations that can be carried out on a lattice and bring it back to itself. These operations are called symmetry operations.

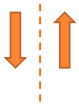
Types of symmetry operation

Translation --- Translation vector, $\vec{T}$

Rotation --- 2π, $^{2\pi}/_{2}$, $^{2\pi}/_{3}$, $^{2\pi}/_{4}$, and $^{2\pi}/_{6}$.

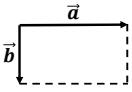
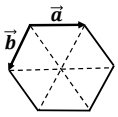
Mirror reflection ----

Inversion --- Rotation by π, followed by a reflection in a plane normal to the rotation axis.

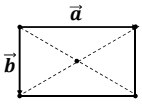


Two dimensional lattice types

There are five distinct lattice types in 2D.

Square lattice	Rectangular lattice	Hexagonal lattice
		
$a = b$	$a \neq b$	$a = b$
$\varphi = 90°$	$\varphi = 90°$	$\varphi = 120°$

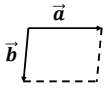
Centered rectangular lattice



$a \neq b$

$\varphi = 90°$

Oblique lattice



$a \neq b$

$\varphi \neq 90°$

Let's label different symmetry operations as follow:

Rotation by π (180°)

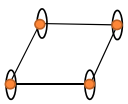
Rotation by $^{2\pi}/_{3}$ (120°)

Rotation by $^{\pi}/_{2}$ (90°)

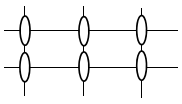
Rotation by $^{\pi}/_{3}$ (60°)

Mirror reflection

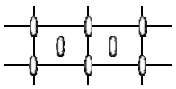
(a) Oblique



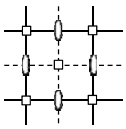
(b) Rectangular



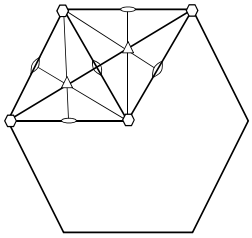
(c) Centered Rectangular



(d) Square lattice



(e) Hexagonal lattice (2D)



Bravais Lattice

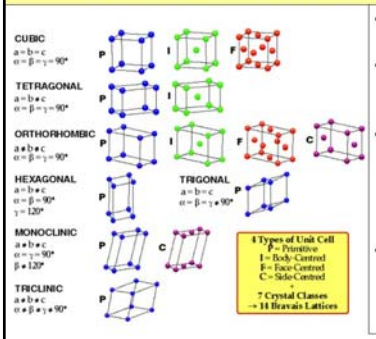
The simplest type of lattice is called a Bravais lattice. A Bravais lattice is an infinite array of discrete points which have position vectors $\vec{R}$

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

Where $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$ are primitive vectors and n_1, n_2, and n_3 are integers.

In 2D, there are 5 Bravais lattice types and in 3D there are 14 Bravais lattice types.

What are crystals?
Bravais Lattices and Space Groups



- 7 crystal systems
- 14 Bravais lattice systems
- Space group = Lattice identifier + known symmetry relationships
- Molecules within the crystal will most likely pack with symmetry

14 plane lattices + 32 point groups
→ 230 Space groups

Crystal Class	Bravais Lattices	Point Groups
Triclinic	P	1, $\bar{1}$
Monoclinic	P, C	2, m, 2/m
Orthorhombic	P, C, F, I	222, mm2, 2/m 2/m 2/m
Trigonal	P, R	3, $\bar{3}$, 32, 3m, $\bar{3}$2/m
Hexagonal	P	6, $\bar{6}$, 6/m, 622, 6mm, $\bar{6}$m2, 6/m 2/m 2/m
Tetragonal	P, I	4, $\bar{4}$, 4/m, 422, 4mm, $\bar{4}$2m, 4/m 2/m 2/m
Isometric	P, F, I	23, 2/m$\bar{3}$, 432, $\bar{4}$3m, 4/m$\bar{3}$2/m

Index system for crystal planes (Miller Index)

The most widely used index system in crystallography is called Miller index, the notation is (*h, k, l*) where *h, k, l* are integers.

To determine Miller index:

(1) Find the intercepts of the plane with the axes $\vec{x}$, $\vec{y}$, and $\vec{z}$ in terms of lattice constants.
(2) Take the reciprocal of those numbers and reduce them to three integers.

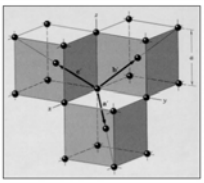
To express a set of equivalent planes, we use curly braket, such as {100} = (100), (010), (001), ($\bar{1}$00), (0$\bar{1}$0), (00$\bar{1}$).

Index system for the directions

[*h k l*] is the direction of a vector whose components along $\vec{x}$, $\vec{y}$, and $\vec{z}$ axes have the ratio of *h:k:l* .

Primitive cell of important lattice structures

Body-centered cubic (BCC)



- Primitive translation vectors

$$\vec{a}' = \frac{a}{2}(\hat{x} + \hat{y} - \hat{z})$$

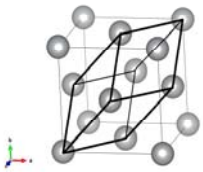
$$\vec{b}' = \frac{a}{2}(-\hat{x} + \hat{y} + \hat{z})$$

$$\vec{c}' = \frac{a}{2}(\hat{x} - \hat{y} + \hat{z})$$

orthogonal vectors of unit length

Face-centered cubic (fcc)

Primitive translation vectors



$$\vec{a}_1 = \frac{1}{2}a(\hat{x} + \hat{y})$$

$$\vec{a}_2 = \frac{1}{2}a(\hat{y} + \hat{z})$$

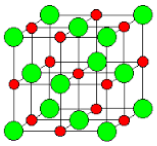
$$\vec{a}_3 = \frac{1}{2}a(\hat{z} + \hat{x})$$

The rhombohedral primitive cell of the fcc crystal. The primitive translation vectors connect the lattice point at the origin with lattice points at the face centers.

Simple crystal structures

Sodium Chloride

The lattice is fcc structure, the basis consists of two atoms (Na and Cl). There are 4 units of NaCl in a conventional cell.



Position of Na

(½ ½ ½), (0 0 ½), (0 ½ 0), (½, 0, 0), (1, ½, 0), (½, 1, 0), (1, 0, ½), (½, 0, 1), (0, ½, 1), (0, 1, ½), (1, 1, ½), (1, ½, 1), (½, 1, 1).

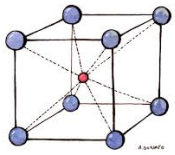
Position of Cl

(0, 0, 0), (0, 1, 0), (½, ½, 0), (1, 0, 0), (1, 1, 0), (1, ½, ½), (½, 1, ½), (0, ½, ½), (0 0 1), (1 0 1) (1 1 1), (0 1 1), (½, ½, 1), (½, 0, ½).

Other crystals which have NaCl structure include: LiH, KCl, PbS, AgBr, MgO, and KBr etc.

Cesium Chloride

The primitive cell is a simple cubic. There are two atoms per basis (One Cs and one Cl)



Cesium position

(0 0 0), (1 0 0), (1 1 0), (0 1 0) (1 0 1), (0 0 1), (1 1 1), (0 1 1)

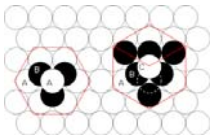
Chlorine position

(½, ½, ½).

Other crystals which have this structure include: BeCu, AlNi, TlI, and LiHg.

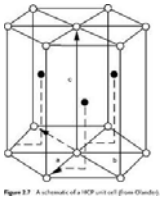
Hexagonal closed-packed structure

There are infinite number of ways to arrange identical hard spheres in a closed-packed structure. The most often found are fcc and hcp structures.



If the stacking is arranged in ABABAB… then the structure is hcp. If the 3rd layer goes over C location, the sequence is ABCABCABC… then the structure is fcc.

The hcp structure has a hexagonal primitive cell with two atoms per unit cell. The volume of the primitive cell is given by $V = |\vec{a}_1 \times \vec{a}_2 \cdot \vec{c}|$, one atom at (0, 0, 0) and the other at (2/3, 1/3, ½), where $|\vec{a}_1| = |\vec{a}_2|$ and $\varphi = 120°$.

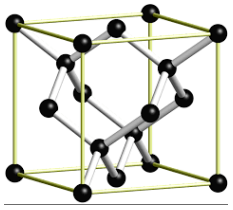


For ideal hcp structure, c=1.633a. For real hcp crystal, the c/a ratio may deviate from 1.633.

Examples: He, Be, Mg, Ti, Zn, Cd, Co, Y, Zr, Gd, Lu.

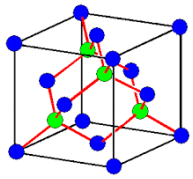
Diamond structure

Diamond structure has a fcc lattice with two identical atoms associated with the basis, one at (0, 0, 0) and one at (¼, ¼, ¼). The filling factor of diamond structure is only 0.34, much less than fcc lattice. All bonds in diamond structure are covalent tetrahedral bonding.



Cubic Zinc Sulfide structure

It has a fcc lattice with two different atoms per basis, one at (0, 0, 0) and the other one at (¼, ¼, ¼).



Diamond structure possesses a center of inversion symmetry, but Zinc Sufide does not.

Diamond structure

CC … CC … CC … CC … CC

Zinc Sulfide structure

ZnS … ZnS … ZnS … ZnS … ZnS