II. Crystal Structures I

Key ideas to pay attention to:

- Description: Lattice + Basis of atoms
- Lattices: finite number of types (exploit periodicity and symmetry)
- How to describe a lattice?
  - $\vec{a}_1, \vec{a}_2, \vec{a}_3$
  - primitive unit cell
  - Wigner-Seitz cell
  - conventional cell
  - $\vec{R}$
- Get yourself familiar with
  - description of SC, FCC, BCC lattices (3D)
  - hexagonal lattice (2D), square lattice (2D)

II. Crystal Structures I

A. Key idea: Lattice + Basis

How could one describe the following 2D periodic structure?
[ideas can be generalized easily to 3D]

• = some atom

an infinite array

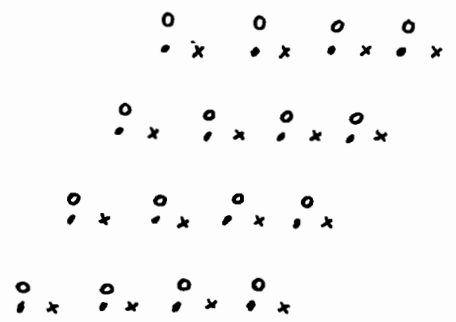
An infinite repetition of identical structural units in space, and the unit consists of one atom.

Ideal crystal:
There is an underlying periodic lattice.

In this example, the atoms can be regarded as sitting on the sites of a regular lattice; OR as sitting on equivalent positions of a regular lattice.

The lattice is a mathematical description. There could be no atoms on the lattice sites.

Next, we consider another 2D crystal of the form:



where o = atom A
• = atom B
x = atom C

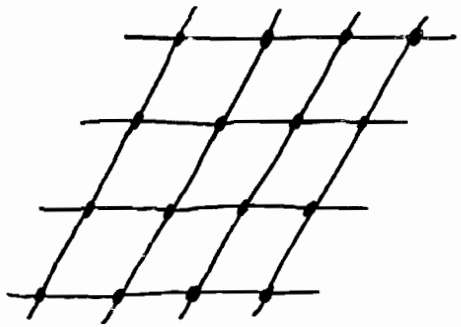
We would say:
this is an infinite repetition of identical structure units in space, and the unit here consists of 3 atoms (:x). [smallest unit]

In this example, the A, B, and C atoms sit on equivalent positions of an infinite underlying lattice, i.e., the crystal structure can be described as decorating each site (or each unit) of the underlying lattice with the same group of atoms. We call the group of atoms the basis.

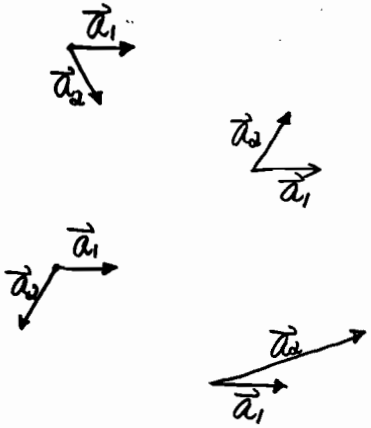
∴ We have:

Lattice (Mathematical description of periodicity in space) + Basis (where the atoms sit in the lattice) = Crystal Structure

Underlying lattice of examples on p. II-①, II-②



Some possible choices of primitive vectors:



We will discuss the ideas of Lattice and Basis one by one.

B. Bravais Lattices

– The mathematical description of the underlying lattice.

- A Bravais lattice in 3D is an infinite array of discrete points whose position vectors $\vec{R}$ are of the form:

$$\vec{R} = u_1\vec{a}_1 + u_2\vec{a}_2 + u_3\vec{a}_3$$

where u_1, u_2, u_3 are arbitrary integers, i.e.,

$u_i = 0, \pm 1, \pm 2, \pm 3, \ldots$

The vectors $\vec{a}_1, \vec{a}_2, \vec{a}_3$ are non-coplanar.
They are called primitive translation vectors, or simply primitive vectors.

$\vec{R}$ is called a lattice vector.

Note that any two lattice points are connected by a lattice vector.

Remark: We use $\vec{a}_1, \vec{a}_2, \vec{a}_3$ for the primitive translation vectors. In some books, e.g. in Christman's book, $\vec{a}, \vec{b}, \vec{c}$ are used. Kittel used $\vec{\tau}_1, \vec{\tau}_2, \vec{\tau}_3$.

More on primitive vectors

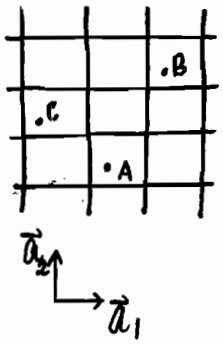
- There are many choices of $\vec{a}_1, \vec{a}_2, \vec{a}_3$ for a given lattice. As long as ALL the lattice points are generated by $u_1\vec{a}_1 + u_2\vec{a}_2 + u_3\vec{a}_3$, the choice is OK!
  (u_1, u_2, u_3 must be integers)
- $\vec{a}_1, \vec{a}_2, \vec{a}_3$ are often used to define the crystal axes.
- $\vec{a}_1, \vec{a}_2, \vec{a}_3$ give the smallest translations, when applied repeatedly, that generate the desired lattice.

Periodicity:

- There are (infinitely) many lattice vectors $\vec{R}$.
- Positions (not necessarily lattice sites) connected by a lattice vector $\vec{R}$ are equivalent – meaning that they have the same environment.

$\vec{a}_1, \vec{a}_2, \vec{a}_3$ and thus the set $\{\vec{R}\}$ of all lattice vectors characterize the discrete translation symmetry of a lattice.

2D square lattice

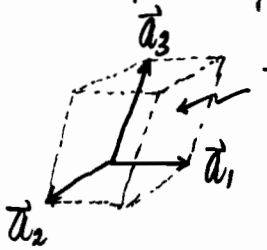


A, B, C are equivalent positions.

- A and B are connected by $\vec{a}_1 + 2\vec{a}_2$
- B and C are connected by $-2\vec{a}_1 - \vec{a}_2$
- A and C are connected by $-\vec{a}_1 + \vec{a}_2$

C. Primitive cell (Primitive unit cell)

$\vec{a}_1, \vec{a}_2, \vec{a}_3$ form a parallelepiped, called a primitive cell



the volume forms a primitive cell.

$$\Omega_c = \text{volume of primitive cell} = |\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)|$$

↖ does NOT depend on the choice of $\vec{a}_1, \vec{a}_2, \vec{a}_3$.

In 2D lattices, we have $\vec{a}_1, \vec{a}_2$. We may introduce a $\vec{a}_3 = \hat{z}$, and then $|\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)|$ or $|\vec{a}_3 \cdot (\vec{a}_1 \times \vec{a}_2)|$ gives the area of the 2D primitive cell.

- There is always one lattice point per permitive cell.
- By stacking up primitive cells, one can fill all space!
  - stacking up ↕ translations through $\{\vec{R}\}$
  - fill all space ↕ No voids AND No overlaps.

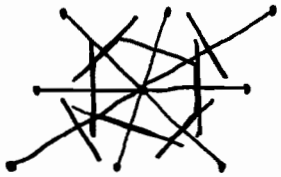
The Wigner-Seitz Primitive Cell

- It is a special primitive cell that reflects the full symmetry of the Bravais lattice.

Definition:

The Wigner-Seitz cell about a lattice point is the region of space that is closer to that point than to any other lattice point.

Sounds Complicated? Not so!



3-Step Construction+

① Take a lattice point, draw lines connecting the point to all nearby lattice points.

② Bisect these lines with orthogonal planes.

③ Construct the smallest polyhedron that contains the point.

Co-ordination number

Number of nearest neighbors.

Positions in the Primitive cell – useful in locating atoms in a basis

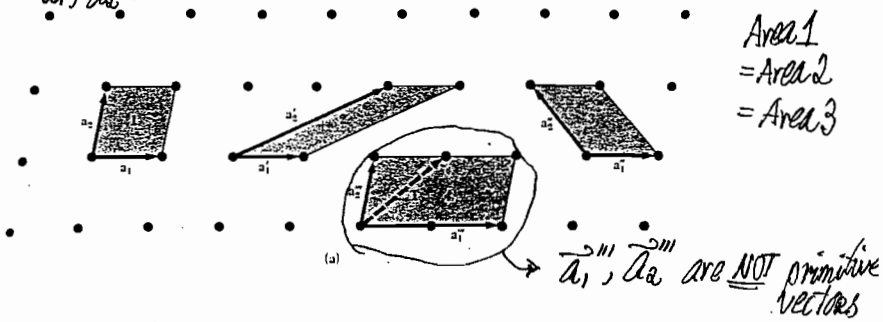
Let $\vec{r}$ = position of a point within the primitive cell (taking cell corner as origin)

then $\boxed{\vec{r} = x_1\vec{a}_1 + x_2\vec{a}_2 + x_3\vec{a}_3, \quad 0 \le x_1, x_2, x_3 \le 1}$

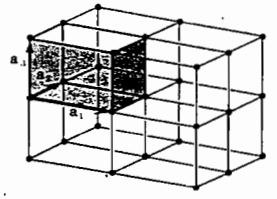
+ We are doing the construction in real space and the resultant polyhedron is the Wigner-Seitz cell. Later in the course, we shall do a similar construction in k-space (reciprocal space) to get the Brillouin Zone.

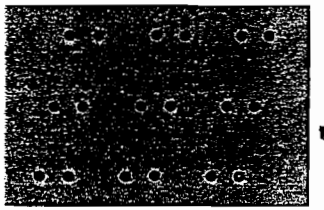
Let's recap what we have so far:

2D: $\left.\begin{matrix}\vec{a}_1, \vec{a}_2,\\ \vec{a}_1', \vec{a}_2',\\ \vec{a}_1'', \vec{a}_2''\end{matrix}\right\}$ are possible choices of primitive translation vectors



3D





basis of 2 atoms per primitive cell

(b) (c)

From Kittel

Lattice points of a space lattice in two dimensions. All pairs of vectors a_1, a_2 are translation vectors of the lattice. But a_1''', a_2''' are not primitive translation vectors because we cannot form the lattice translation $\mathcal{R}$ from integral combinations of a_1''' and a_2'''. All other pairs shown of a_1 and a_2 may be taken as the primitive translation vectors of the lattice. The parallelograms 1, 2, 3 are equal in area and any of them could be taken as the primitive cell. The parallelogram 4 has twice the area of a primitive cell.

Primitive cell of a space lattice in three dimensions.

Suppose these points are identical atoms: sketch in on the figure a set of lattice points, a choice of primitive axes, a primitive cell, and the basis of atoms associated with a lattice point.

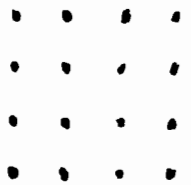
D. Fundamental Types of Lattices

2D: Q: How many possible lattices can one have in 2D?

- Infinite many! Can take arbitrary $|\vec{a}_1|$ and $|\vec{a}_2|$ and the value of angle between the two primitive translation vectors.

However, there are special types of lattices.

- For example, consider the special type of square lattice.



Note: Still infinite many possible square lattices. Why?

- Why is it special?

  Ans: It possesses special symmetries.

  meaning: Some physical operation (e.g., rotation, inversion, etc) that changes the positions of the lattice points, but in such a way the lattice points are at exactly the same places after the operation as before.

e.g. Rotation of 90° ($\frac{\pi}{2}$) about an axis through "x".

After operation, all the points are at the same places as before.

Obviously, rotations of 180°, 270° give back the lattice as well.

Note: $\frac{\pi}{2} = \frac{2\pi}{4}$, we say that "the square lattice possesses a 4-fold rotation axes at the point marked x". The "4" comes from the 4 in $\frac{2\pi}{4}$.

More, we can also rotate about an axis through a lattice point by $\frac{2\pi}{4}$ (90) to get back the square lattice.

Even more, we can rotate about any axis in the the $\hat{y}$-direction passing through a column of points by $\frac{2\pi}{2}$ (180°) to get back the lattice.

There are many other symmetry operations for the 2D square lattice.

It is the symmetry of the lattice that makes it special.

Short-hand notations showing the symmetry elements.†

- Each type of lattice has its specific symmetry elements.
- The mathematics describing periodic lattices is Group theory. We shall not go into details as it is a whole subject by itself. We want to emphasize the points that:

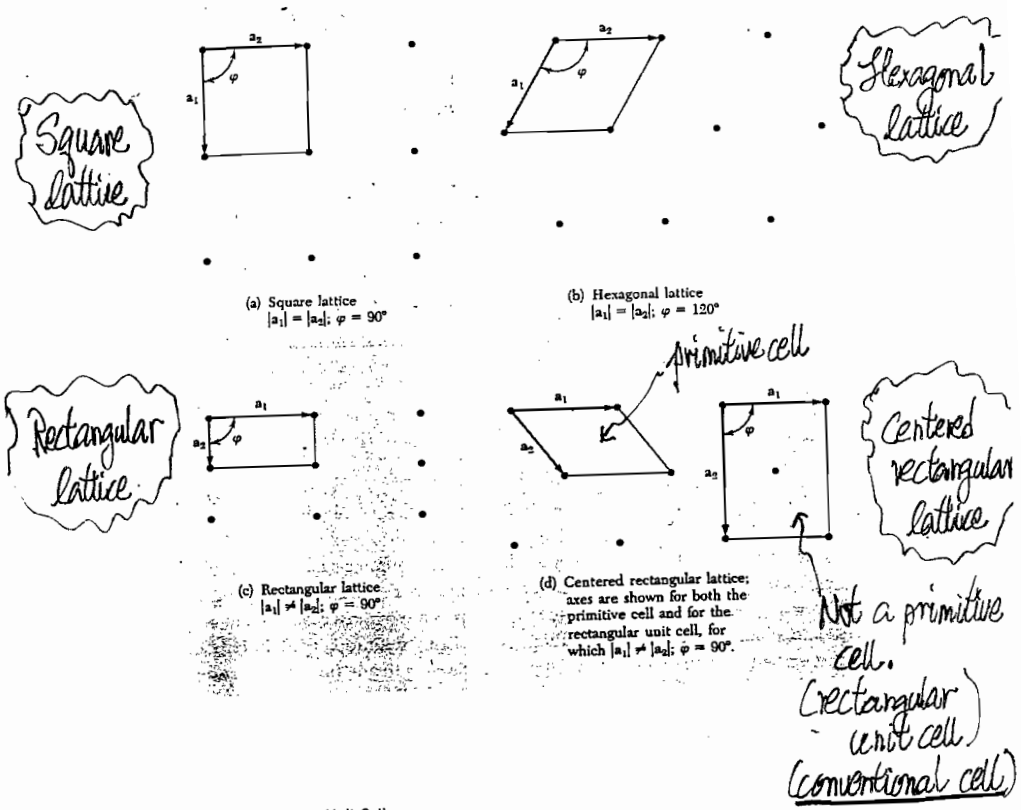
(1) The lattices are classified into types by considering their symmetries.
(2) The relevant mathematics is Group theory.
(3) Mathematicians told us that:
- There are 5 types of lattices in 2D.
- There are 14 types of lattices in 3D.

† The aim here is to point out that a type of lattice is characterized by the symmetry operations, instead of going into the detail of the operations.

The 5 types of lattices in 2D

Square lattice

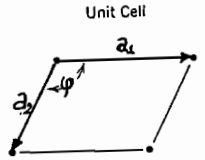
Hexagonal lattice



Rectangular lattice

Centered rectangular lattice

Not a primitive cell. (rectangular unit cell) (conventional cell)

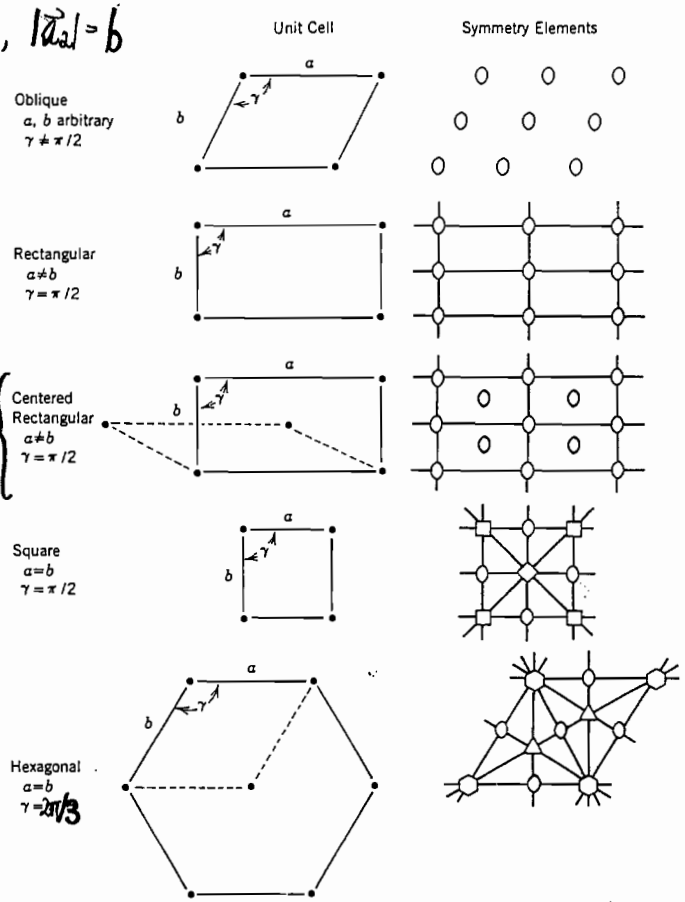


(e) Oblique lattice
$|\vec{a}_1|$, $|\vec{a}_2|$ arbitrary
$\varphi \neq \frac{\pi}{2}$

All crystal structures in 2D must belong to one of these five types of lattices. The actual crystal structure is then described by attaching a basis, which could be quite complicated, to the lattice points, plus the determination of $\vec{a}_1$ and $\vec{a}_2$ (including their magnitudes).

The symmetry elements of the 5 types of lattices in 2D

$|\vec{a}_1| = a$, $|\vec{a}_2| = b$



Note: the rectangle ab is a conventional cell.

Two-dimensional lattices: unit cells and symmetry elements.

Notations

- ⬡ $\frac{2\pi}{2}$ (180°) rotation with axis pointing into the paper.
- □ $\frac{2\pi}{4}$ (90°) rotation with axis pointing into the paper.
- △ $\frac{2\pi}{3}$ (120°) rotation with axis pointing into the paper.
- ／ π (180°) rotation about the line, i.e. mirror line

(See Christman: Sec. 2.2, 2.3)

- Note that there are only 2, 3, 4, 6-fold rotation axes in these lattice types.

Jargon: Bravais lattice is the common phrase for a distinct lattice type.

We say that there are Five Bravais lattices in two dimensions.

Primitive cell with 5-fold symmetry and 7-fold symmetry

Can't fill space without leaving voids by pentagons.

No 5-fold symmetry axis

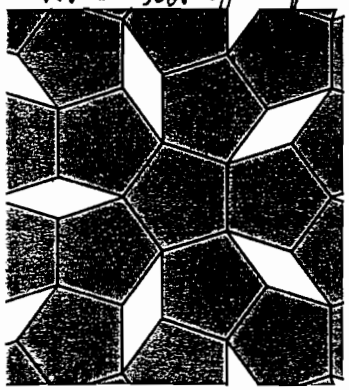


Figure 9a A five-fold axis of symmetry cannot exist in a lattice because it is not possible to fill all space with a connected array of pentagons.

Voids

Can't fill space without overlaping by 7-gons

No 7-fold symmetry axis

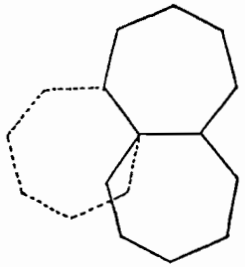
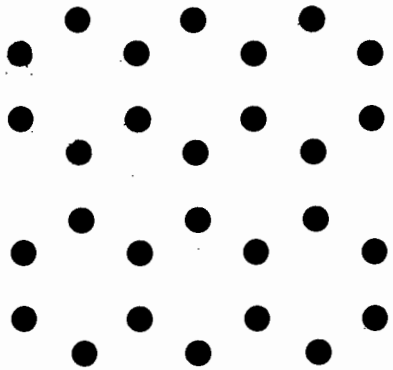


Figure 9b Kepler's demonstration (*Harmonice mundi*, 1619) that a seven-fold axis of symmetry cannot exist in a lattice. (*Gesammelte Werke*, Vol. 6, Beck, Munich, 1940.)

Overlaps

How about this 2D structure?

• = carbon



This is a very hot topic in physics now!

This is called graphene (a monolayer of carbon atoms).

Free-standing graphene was found in 2004

(K.S. Novoselov et al., Science 306, 666 (2004);
Proc. Natl. Acad. Sci. 102, 10451 (2005))

For an introduction, see Geim and Novoselov, "The rise of graphene", Nature materials 6, 183 (2007).

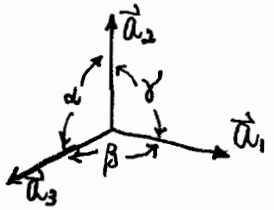
THREE DIMENSIONS (3D)

- There are 14 Bravais lattices in 3D.
- They are classified according to the symmetry.
- They can be further classified into 7 systems.

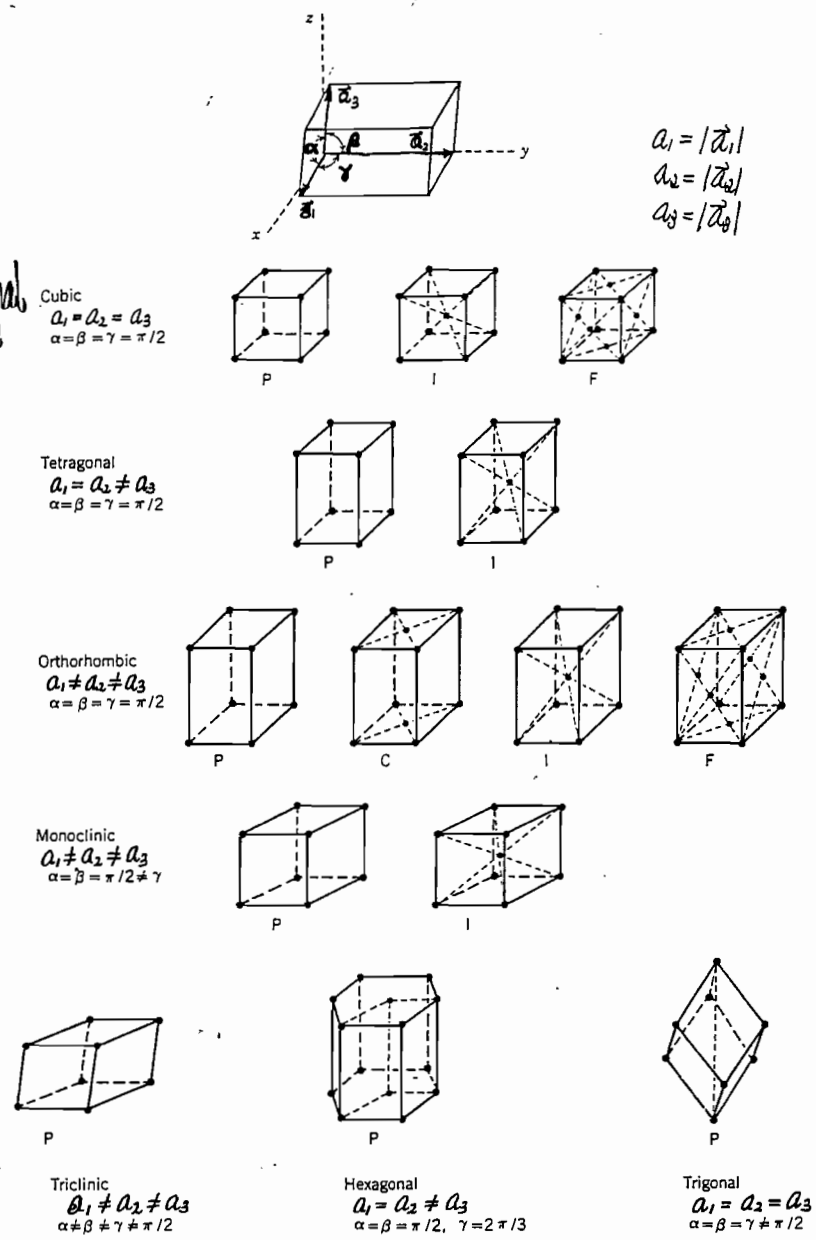
The 14 lattice types in three dimensions

System	Number of lattices	Restrictions on conventional cell axes and angles
Triclinic	1	$a_1 \neq a_2 \neq a_3$ $\alpha \neq \beta \neq \gamma$
Monoclinic	2	$a_1 \neq a_2 \neq a_3$ $\alpha = \gamma = 90° \neq \beta$
Orthorhombic	4	$a_1 \neq a_2 \neq a_3$ $\alpha = \beta = \gamma = 90°$
Tetragonal	2	$a_1 = a_2 \neq a_3$ $\alpha = \beta = \gamma = 90°$
→ Cubic	3	$a_1 = a_2 = a_3$ $\alpha = \beta = \gamma = 90°$
Trigonal	1	$a_1 = a_2 = a_3$ $\alpha = \beta = \gamma < 120°, \neq 90°$
Hexagonal	1	$a_1 = a_2 \neq a_3$ $\alpha = \beta = 90°$ $\gamma = 120°$

conventional cell



- In 3D, we obviously need $\vec{a}_1, \vec{a}_2, \vec{a}_3$
- Then there are 3 angles specifying their relative orientations



The 7 three-dimensional lattice systems and 14 Bravais lattices. [redacted]

Remark

- Sometimes, due to historial reason and conventions, i.e. generation by generation people just keep on using it, a bigger cell (called the conventional unit cell) is used to describe some lattices. Usually, the convention unit cell, which contains more than one lattice points, displays and emphasizes a special character of the lattice's symmetries.

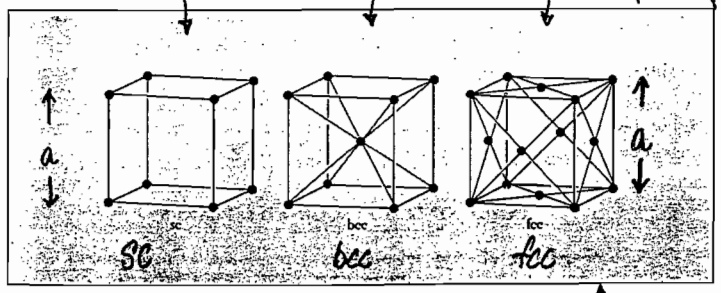
  Examples:

  - See the conventional unit cell of a centered-rectangular lattice in 2D on p. II-(13).
  - See the conventional unit cells of body-centered cubic lattice and face-centered cubic lattice on p. II-(18).

E. Let's focus on the 3 lattices in the Cubic system

primitive cell

conventional cells (more than one lattice points per cell, but show the cubic character)



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

some metals take on bcc structure

Many semiconductors take on fcc structure

Characteristics of cubic lattices

	Simple	Body-centered	Face-centered
Volume, conventional cell	a^3	a^3	a^3
Lattice points per cell	1	2	4
Volume, primitive cell	a^3	$\frac{1}{2}a^3$	$\frac{1}{4}a^3$
Lattice points per unit volume	$1/a^3$	$2/a^3$	$4/a^3$
Number of nearest neighbors[a]	6	8	12
Nearest-neighbor distance	a	$3^{1/2}a/2 = 0.866a$	$a/2^{1/2} = 0.707a$
Number of second neighbors	12	6	6
Second neighbor distance	$2^{1/2}a$	a	a
Packing fraction[b]	$\frac{1}{6}\pi$ $=0.524$	$\frac{1}{8}\pi\sqrt{3}$ $=0.680$	$\frac{1}{6}\pi\sqrt{2}$ $=0.740$

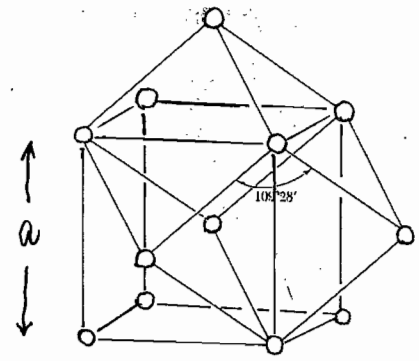
• Simple cubic (sc)

An obvious choice of the primitive vectors is:

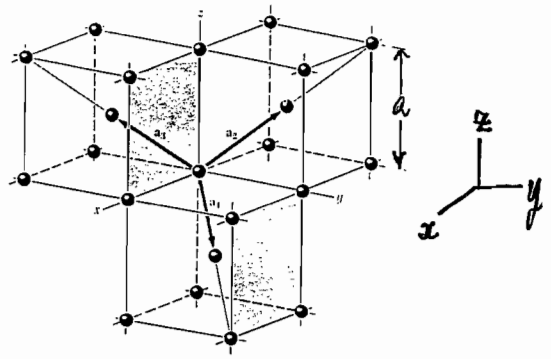
$\vec{a}_1 = a\hat{x}$, $\vec{a}_2 = a\hat{y}$, $\vec{a}_3 = a\hat{z}$

The cube shown above is a primitive cell.

• Body-centered cubic (bcc)



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



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

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

a = edge of the conventional cell ← Databook usually gives value of a

- An obvious choice of the primitive translation vectors is:
  (i) choose a lattice point, (ii) draw vectors to 3 nearest neighbors.

bcc
$$\begin{cases} \vec{a}_1 = \frac{a}{2}(\hat{x} + \hat{y} - \hat{z}) \\ \vec{a}_2 = \frac{a}{2}(-\hat{x} + \hat{y} + \hat{z}) \\ \vec{a}_3 = \frac{a}{2}(\hat{x} - \hat{y} + \hat{z}) \end{cases}$$

Volume of primitive cell
$= |\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)|$
$= \frac{a^3}{2}$

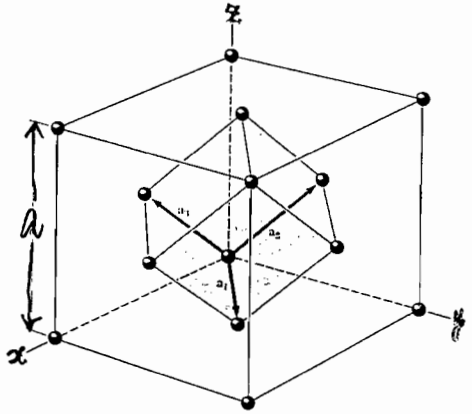
- Conventional cell has 2 lattice pts.

nearest neighbors = 8

Note: The Group I simple metals (Na, K) have bcc structure.

• Face-centered cubic (fcc)

Conventional cell has 4 lattice pts.



The rhombohedral primitive cell of the face-centered cubic crystal. The primitive translation vectors a_1, a_2, a_3 connect the lattice point at the origin with lattice points at the face centers. As drawn, the primitive vectors are:

$a_1 = \frac{1}{2}a(\hat{x} + \hat{y})$; $a_2 = \frac{1}{2}a(\hat{y} + \hat{z})$; $a_3 = \frac{1}{2}a(\hat{z} + \hat{x})$.

The angles between the axes are 60°. Here $\hat{x}$, $\hat{y}$, $\hat{z}$ are the Cartesian unit vectors.

• Primitive translation vectors:
(i) choose a pt.
(ii) draw vectors to 3 nearest neighbors

Volume of primitive cell
$= |\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)|$
$= \frac{a^3}{4}$

nearest neighbors = 12

Note: a^3 = volume of conventional cell

A popular choice is:

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

• Note: Some metals (e.g. Ag, Al, Au, Cu) have fcc structure.
fcc structure is also important in describing semiconductors (diamond, zinc blende structures).
(See Christman: Sec. 2.3) (Kittel: Ch. 1)

• Let's consider the lattice vectors $\vec{R}$ in cubic system.

SC: $\vec{a}_1 = a\hat{x}$, $\vec{a}_2 = a\hat{y}$, $\vec{a}_3 = a\hat{z}$

$\vec{R} = u_1\vec{a}_1 + u_2\vec{a}_2 + u_3\vec{a}_3$
$= a(u_1\hat{x} + u_2\hat{y} + u_3\hat{z})$

(u_1, u_2, u_3 are integers, $0, \pm1, \pm2, \ldots$)

BCC: $\vec{a}_1 = \frac{a}{2}(\hat{x} + \hat{y} - \hat{z})$; $\vec{a}_2 = \frac{a}{2}(-\hat{x} + \hat{y} + \hat{z})$; $\vec{a}_3 = \frac{a}{2}(\hat{x} - \hat{y} + \hat{z})$

$\vec{R} = \underbrace{\frac{a}{2}}_{\text{a length}}[\underbrace{(u_1 - u_2 + u_3)}_{n_1}\hat{x} + \underbrace{(u_1 + u_2 - u_3)}_{n_2}\hat{y} + \underbrace{(-u_1 + u_2 + u_3)}_{n_3}\hat{z}]$

for $\vec{R}$ expressed in this form

Note: n_1, n_2, n_3 have the properties:

$n_1 - n_2 = -2u_2 + 2u_3 =$ even

$n_2 - n_3 = 2u_1 - 2u_3 =$ even

∴ n_1, n_2, n_3 are either all even or all odd for bcc

FCC: $\vec{a}_1 = \frac{a}{2}(\hat{x} + \hat{y})$; $\vec{a}_2 = \frac{a}{2}(\hat{y} + \hat{z})$; $\vec{a}_3 = \frac{a}{2}(\hat{z} + \hat{x})$

$\vec{R} = \frac{a}{2}[(u_1 + u_3)\hat{x} + (u_1 + u_2)\hat{y} + (u_2 + u_3)\hat{z}]$
$= \frac{a}{2}[n_1\hat{x} + n_2\hat{y} + n_3\hat{z}]$

for $\vec{R}$ expressed in this form

Note: n_1, n_2, n_3 satisfy the condition:

$n_1 + n_2 + n_3 = 2\cdot(u_1 + u_2 + u_3) =$ even for fcc

Can we work backward?

Q: If the lattice vectors of a Bravais lattice have the form $\vec{R} = a[n_1\hat{x} + n_2\hat{y} + n_3\hat{z}]$ with $n_1+n_2+n_3 =$ even, identify the Bravais lattice type.

Idea: Try to express $\vec{R}$ in terms of $\vec{a}_1, \vec{a}_2, \vec{a}_3$ and then identify the lattice type based on the primitive vectors.

Write $n_1+n_2+n_3 = 2N$ (even) $\Rightarrow n_3 = 2N - n_1 - n_2$

$$\frac{\vec{R}}{a} = n_1\hat{x} + n_2\hat{y} + (2N - n_1 - n_2)\hat{z}$$

[Put $N - n_1 = m_1$; $N - n_2 = m_2$]

$$= (N-m_1)\hat{x} + (N-m_2)\hat{y} + (m_1+m_2)\hat{z}$$

[Put $N - m_1 - m_2 = n$]

$$= (n+m_2)\hat{x} + (n+m_1)\hat{y} + (m_1+m_2)\hat{z}$$

$$= n(\hat{x}+\hat{y}) + m_1(\hat{y}+\hat{z}) + m_2(\hat{z}+\hat{x})$$

$$\therefore \vec{R} = n\underbrace{\frac{(2a)}{2}(\hat{x}+\hat{y})}_{\vec{a}_1} + m_1\underbrace{\frac{(2a)}{2}(\hat{y}+\hat{z})}_{\vec{a}_2} + m_2\underbrace{\frac{(2a)}{2}(\hat{z}+\hat{x})}_{\vec{a}_3}$$

(n: integer; m_1: integer; m_2: integer)

$\vec{R}$ are lattice vectors of a fcc lattice with conventional cell of size $a' = 2a$.

Summary:

1/. Crystal structure = Lattice + Basis
(Lattice: mathematical description reflecting discrete translational symmetry; Basis: where the atoms are in a unit cell)

2/. Although there are infinitely many lattices, they can be classified according to their symmetry properties into types.

3/. In 2D, there are 5 types.

4/. In 3D, there are 14 types.

5/. Lattices are characterized by $\vec{a}_1, \vec{a}_2, \vec{a}_3$ (choice is not unique)

6/. Lattice vectors

$$\vec{R} = u_1\vec{a}_1 + u_2\vec{a}_2 + u_3\vec{a}_3$$

(u_1, u_2, u_3: integers)

give all the lattice points in a lattice
- $\vec{R}$ relates equivalent points

7/. Construction of Wigner-Seitz cell.

8/. Primitive unit cells

9/. The three Bravais lattices in the cubic system

- sc, bcc, fcc
- choice of $\vec{a}_1, \vec{a}_2, \vec{a}_3$
- using conventional (cubic) unit cell to describe bcc and fcc
- Expressing lattice vectors as

  $\vec{R}$ = (length) $[n_1\hat{x} + n_2\hat{y} + n_3\hat{z}]$

  for sc, bcc, fcc and the different requirements on n_1, n_2, n_3 for different lattices.