Technological Applications

CRYSTAL STRUCTURE

Structure of Solid State Materials

Analysis, Understanding & Characterisation

Spectroscopy & Microscopy

Why do we need to know this ?! Useful for what?!

Semiconductors are **SOLID STATE MATERIALS**

Semiconductors are characterised by their **BAND GAP**

Solid state materials have **CRYSTAL STRUCTURES**

The **Band Gap** of a semiconductor influenced by **Crystal Structure & Atomic Size.**

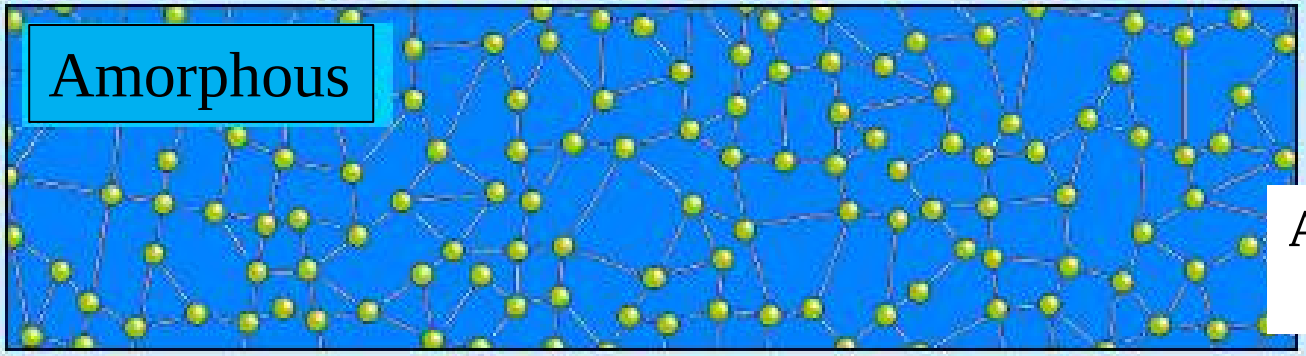
Crystal structures + atomic nr. (size)
define
electric, **magnetic** and **electromagnetic properties** and **behaviour** of **solid state materials**.

Electric, **Magnetic** and **Electromagnetic properties** and **behaviour** of solid state materials are used to understand and characterise a material

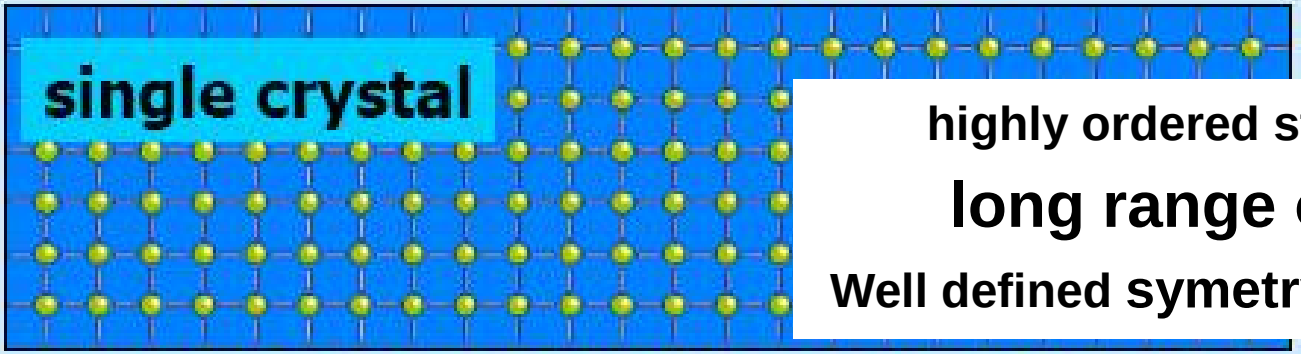
Spectroscopy & **Microscopy Analysis**

and **decide** / **guide**/ **influence** our **decision** on the various possible

Technological Applications



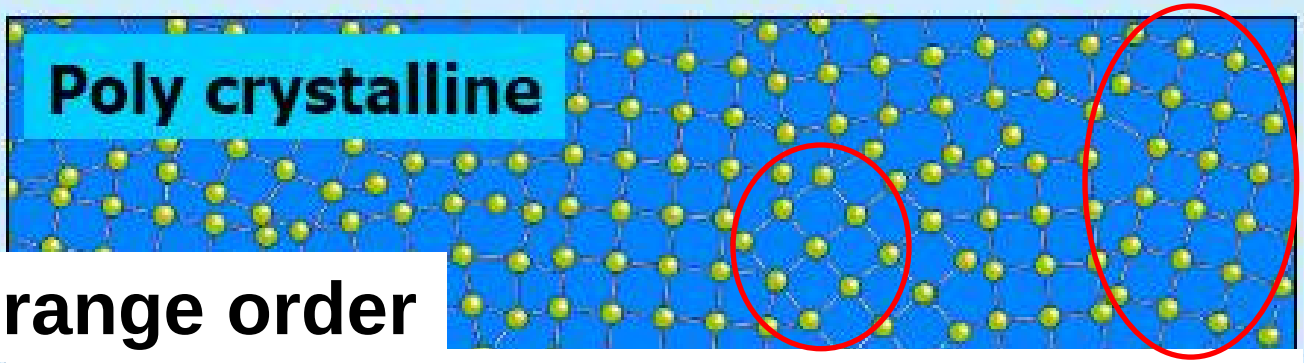
Atoms placed at random
Non-ordered structure



highly ordered structure

long range order

Well defined symetry properties



high degree of short-range order

These materials consist of small crystalline regions with random orientation called grains, separated by grain boundaries.

Chemnitz University of Technology
Semiconductor Physics

- crystals naturally form when liquid material cools down according to particular temperature and pressure conditions;
- crystallization typically occurs in multiple locations simultaneously;
- the poly-crystalline structure is quite common except for materials such as glass which tend to be amorphous; and even in this case we still have some order at the microscale.

Crystals are categorized by their

crystal structure and the underlying lattice.

While some crystals have a single atom placed at each lattice point, most crystals have a:

combination of atoms associated with each **lattice point**.

This combination of atoms is called basis.

Crystal Structure, **Lattice** & lattice point(s), **Basis**

Unit Cell Primitive (unit) cell Bravais Lattice Symmetry Properties

What are they?! How do they relate to each other?!

Atomic Packing factor

Miller indices

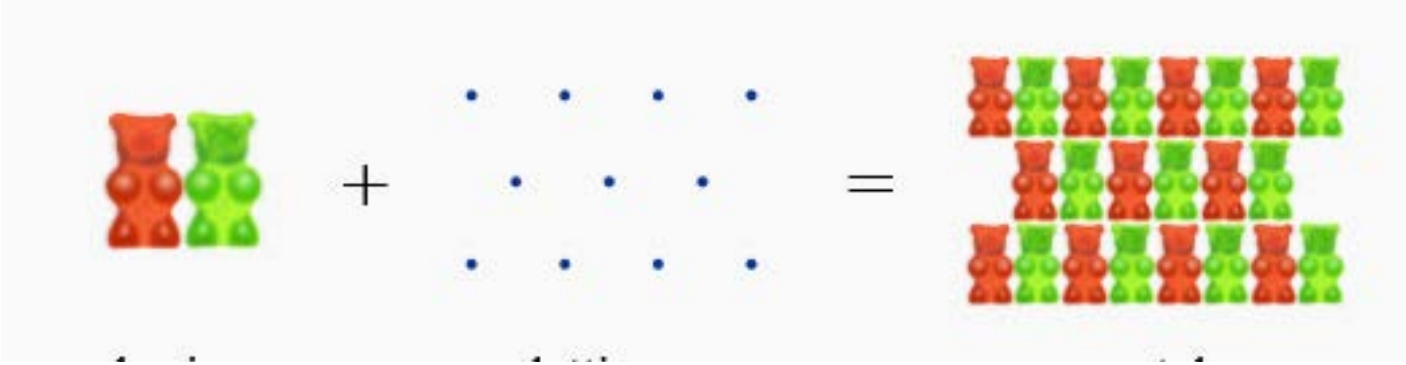
Crystal structure = lattice + basis (?)

ETC… ☺

Crystal = basis + lattice

A crystal is made up of a **periodic arrangement** of one or more structural elements (the basis) repeated at **each lattice point**.

Lattice means '**order**' and is a pure mathematical concept to describe ordered structures. It obeys well defined rules and properties. The concept can be used or applied to varied domains in science.



- **An ideal crystal is therefore an infinite periodical repetition of identical structural elements.**

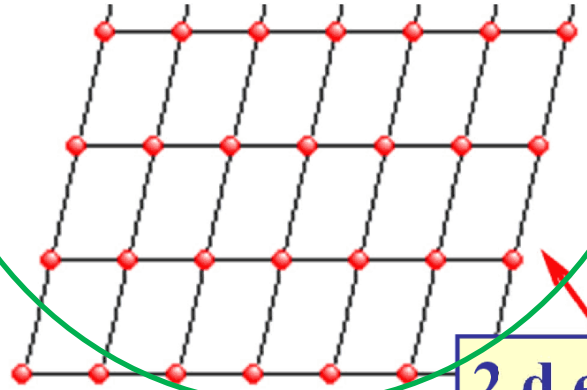
Crystal Lattices

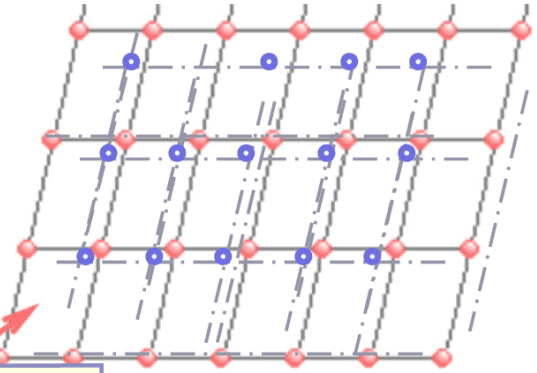
Bravais Lattices
(BL)

All atoms are the same kind
All lattice points are equivalent

Non-Bravais Lattices
(non-BL)

Atoms are of different kinds.
Some lattice points aren't equivalent.
A combination of 2 or more BL





2 d examples

Bravais Lattice merges the concept of **Lattice** (pure mathematical entity) and **Base** (physical entities positioned at the lattice points. It's therefore the *Lattice* concept applied to **ordered Solid State structures**: crystallography

A lattice to be *Bravais type* has to obey additionally to certain criteria:

1. be an infinite array of discrete points in three dimensional space generated by a set of discrete translation operations described by the following vector:

$$\vec{R} = n\vec{u}_1 + m\vec{u}_2 + l\vec{u}_3$$

- n, m, l are integers and represent **lattice points**
- $\vec{u}_1$, $\vec{u}_2$, $\vec{u}_3$ are vectors, called **primitive lattice vectors** along the 3 directions of space.

2. In 3D space a translation of the whole lattice by any *translation vector* given by this vector **leaves the lattice unchanged**.

Lattice points

- *n*, *m*, *l* are integers and represent the lattice points

- **All lattice points are equivalent**, i.e. all properties remain invariant under translations by any vector. Also, an observer sitting on one specific lattice point would see the same environment as when sitting on any other.

- Consequently, the **crystal looks the same** when viewed **from any equivalent lattice point**, namely those separated by the translation of one unit cell (the motif).

Primitive Lattice vectors

- $\vec{u}_1$, $\vec{u}_2$, $\vec{u}_3$ are called **primitive lattice vectors,** lie on different spatial directions and span the lattice.
- the length of these vectors = **lattice constants** = **a**
- for a given lattice the choice of the primitive translation vectors is not unique!
- For any choice of position vector R, the lattice looks exactly the same.

Unit Cell

- A crystal is built up by the **smallest elements** that are **repeated** in **all directions**, **filling the whole space**.

- These elements are called **unit cells** and fulfil the following requirements:

A repetitive arrangement (pure translation) of them can build up the whole crystal without overlaps/gaps.

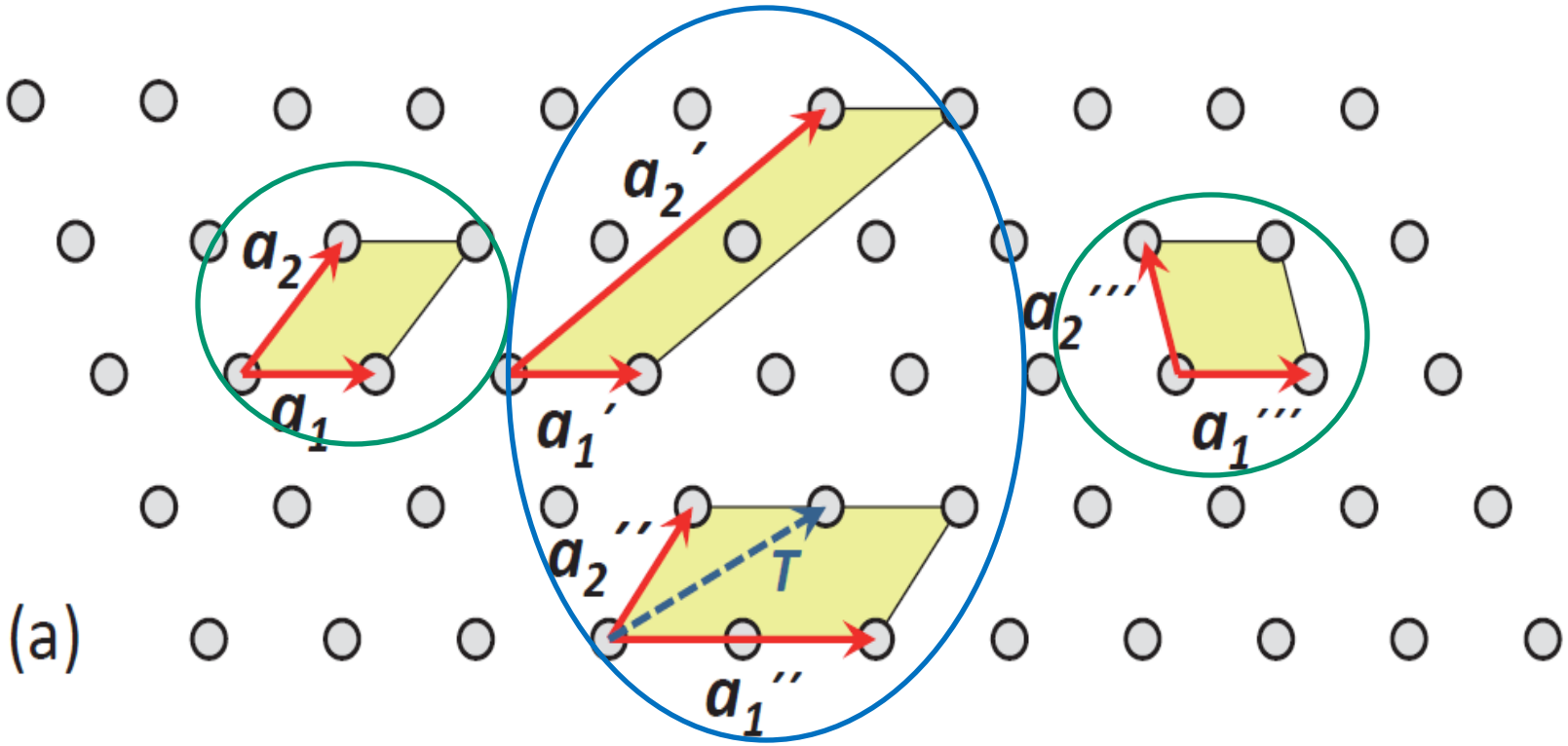
Primitive Unit Cell

A unit cell is considered primitive when:

- is the smallest possible cell
- contains only one lattice point
- can be used to reproduce the entire crystal

- If there is a lattice point at the edge of a cell and thus shared with another cell, it is only counted half (1/2). Accordingly, a point located on the corner of a cube is shared by 8 cubes and would count only 1/8.

Unit Cells: Primitive & non-Primitive



The choice of a unit cell is not unique.

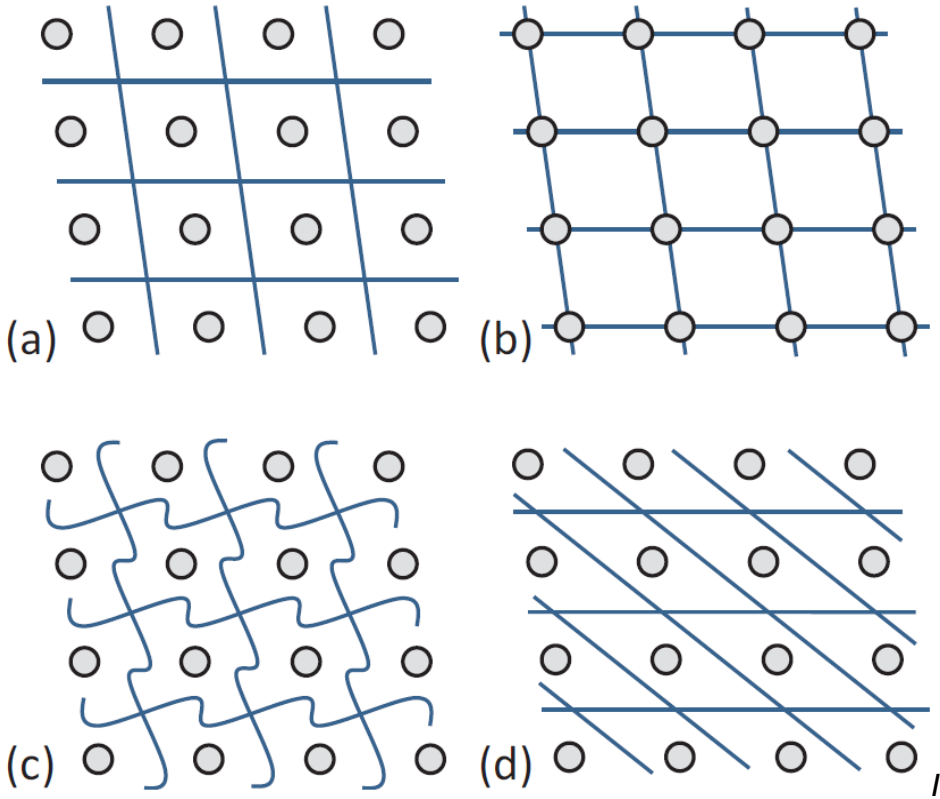
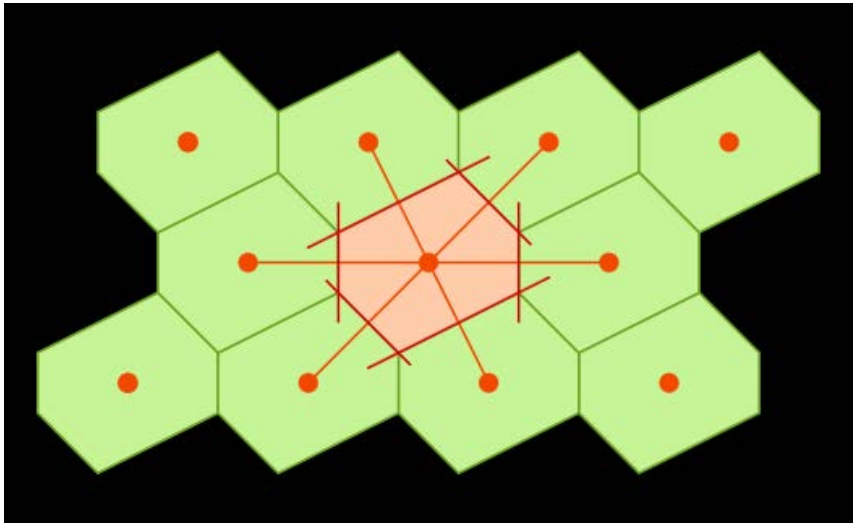


Image source: Gross

- It is convenient to choose the one with the highest level of inner symmetry.

The Wigner-Seitz Cell: Special type of primitive-cells.

The *Wigner-Seitz cell* of a lattice point is defined as the **volume** that encloses all points in space which are closer to this particular **lattice point** than to any other.



Construction

1st step: Choose any lattice point and draw connecting lines to its closest neighbours.

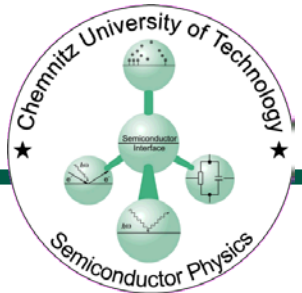
2nd step: Draw the perpendicular bisectors of the connecting lines.

Final result: The enclosed area defined by the intersection of this connecting lines is the Wigner-Seitz cell. It forms a unit cell, i.e. is able to build the whole lattice without gaps/overlaps.

Crystal Systems

Bravais Lattices

Symmetry & Geometry



When **describing spatial arrangements** of objects this is done by using a **coordinate system**: cartesian, cylindrical, spherical, ...

The **choice** of the coordinate system usually **depends** on the **symmetry & geometry** .

It is therefore helpful to classify crystal structures according to their **symmetry**.

Symmetry

During this course we will focus on crystals with discrete **translational symmetry**, i.e. crystals which are formed by the combination of a **Bravais lattice** and a corresponding **basis**.

Besides these we will also make use of ***point symmetries***, i.e. the group of **symmetry operations** that leaves at least **one point unchanged**:

Rotations , Reflections, Inversions
or
any combinations of these

They are the basis of the classification of crystals: we can count the number of axes of rotation and their respective multiplicities in order to compare different crystals in regard of their symmetry.

Symmetry

Symmetry elements
geometric objects consisting of all space points, that do not change their position upon the given symmetry operation.

Basic symmetry operations:
geometric operations that transform the crystal lattice into itself:

E - Identity operation

I – Inversion operation

C_n - n-fold rotation ≡ Rotation by **(2π/n)** radians
[C_2 = π (180°), C_3 = (⅔)π (120°), C_4 = (½)π (90°), C_6 = (⅓)π (60°)]

σ - Reflection symmetry through a plane

S_n - C_n rotation, followed by a **reflection** through a plane ⊥ rotation axis **(improper rotation)**

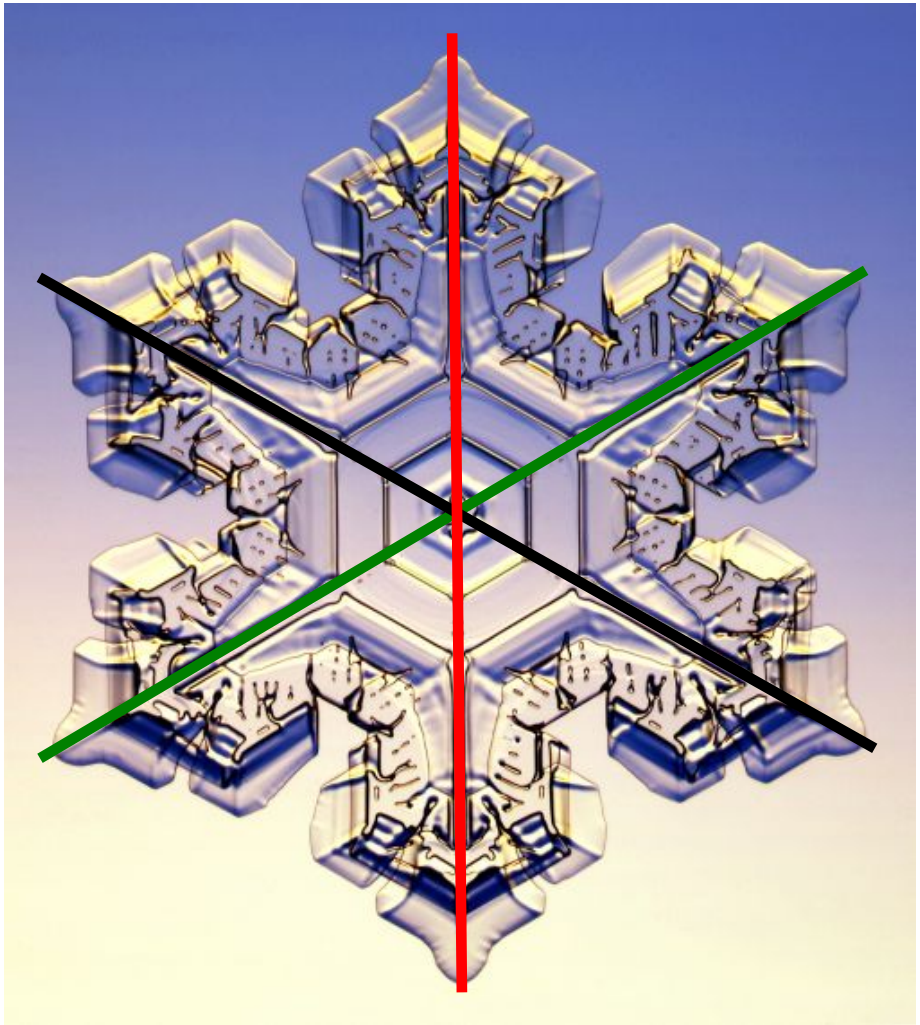
Examples of Basic Symmetry Operations

Rotation

C_n - n-fold rotation

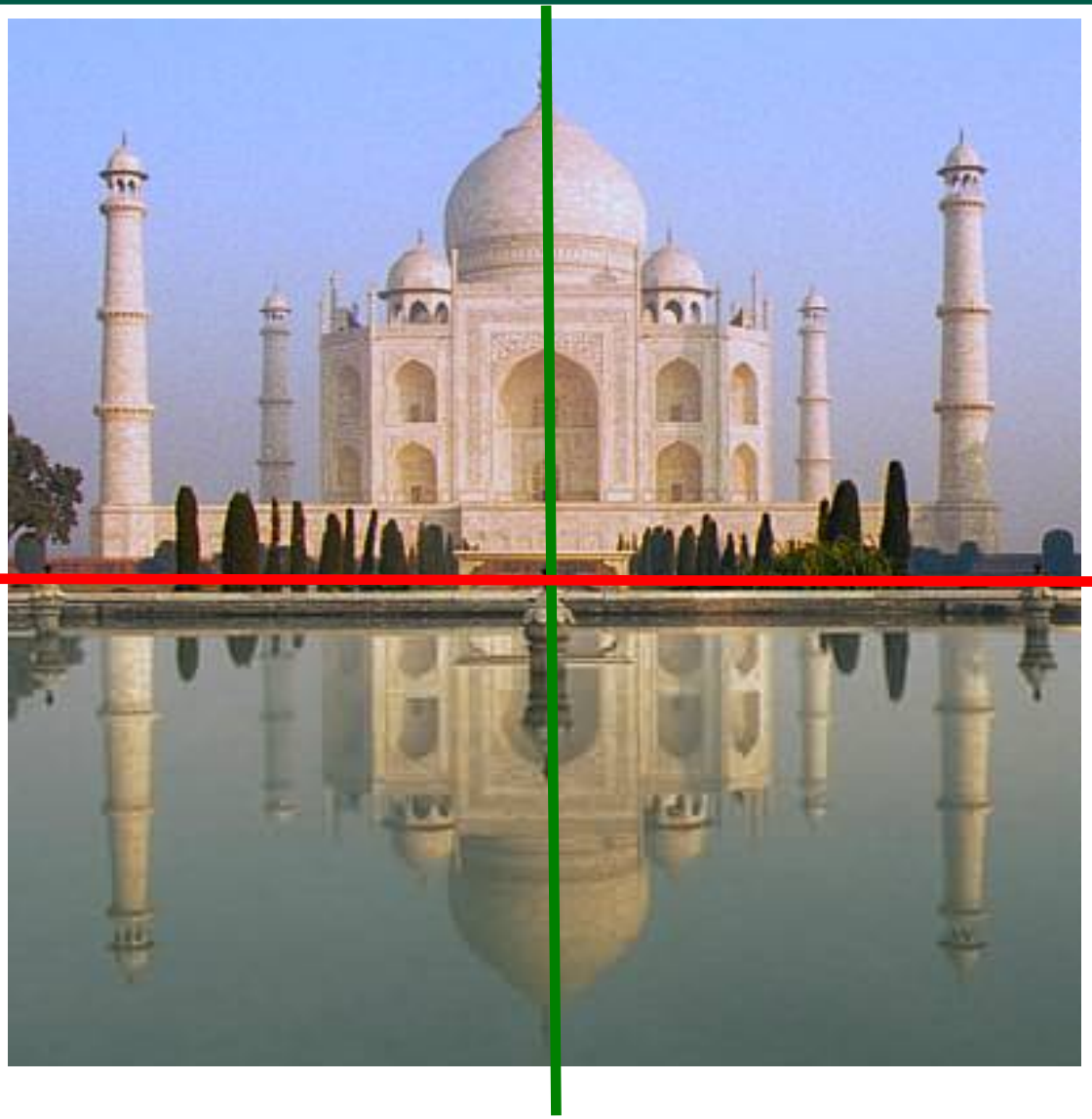
n=?

$C_6 = (⅓)\pi\ (60^\circ)$



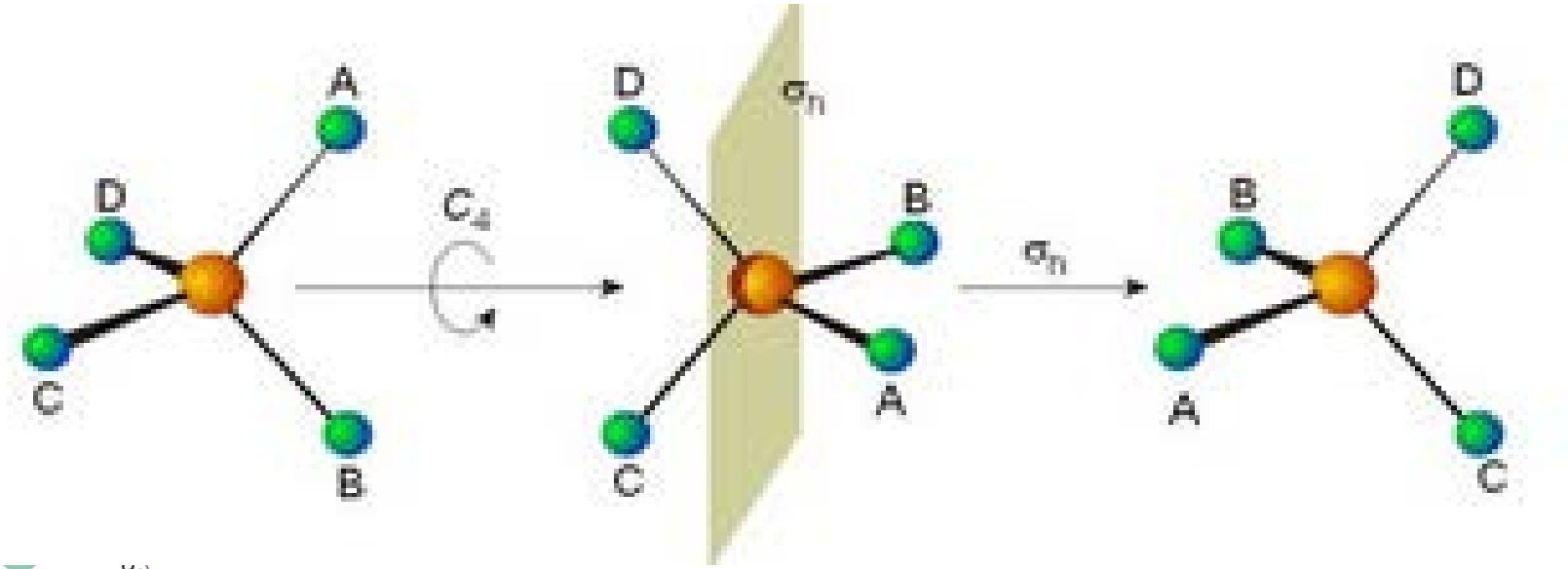
Examples of Basic Symmetry Operations

σ - Reflection
symmetry
through a plane



Examples of Basic Symetry Operations

Sn = Cn rotation – σ reflexion
Improper Rotation



The **Bravais Lattices**

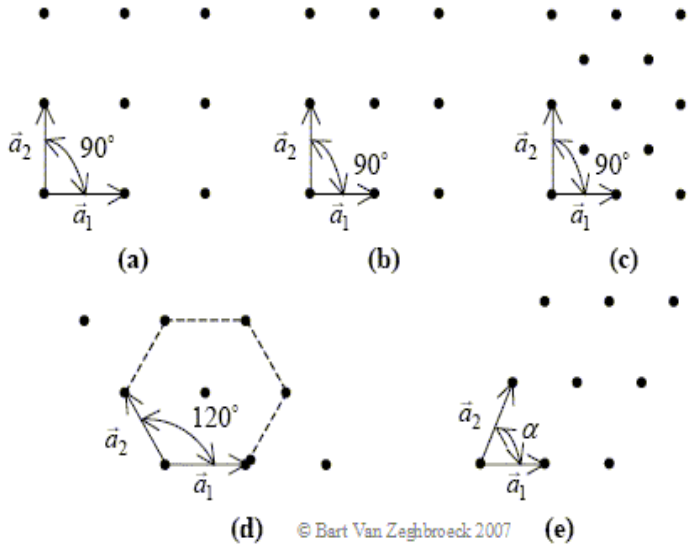
classified with respect to

Symmetry & Geometry

✓ Sometimes it makes sense not to use a primitive unit cell but one which fits better to the symmetry of the problem.

✓ This idea leads to the **5 Bravais Lattices in 2D space** and **14 Bravais Lattices in 3D space** , ordered by the crystal systems.

In **2D**, there are **5 distinct** **Bravais lattices**:



The five Bravais lattices of two-dimensional crystals: (a) square, (b) rectangular, (c) centered rectangular, (d) hexagonal and (e) oblique

Name	Number of Bravais lattices	© Bart Van Zeghbroeck 2007 Conditions
Square	1	$a_1 = a_2$, $\alpha = 90°$
Rectangular	2	$a_1 \neq a_2$, $\alpha = 90°$
Hexagonal	1	$a_1 = a_2$, $\alpha = 120°$
Oblique	1	$a_1 \neq a_2$, $\alpha \neq 120°$, $\alpha \neq 90°$

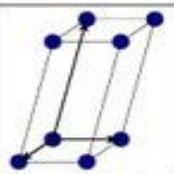
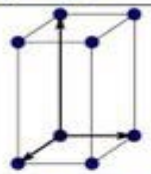
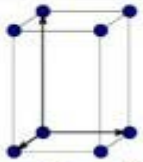
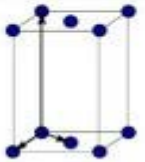
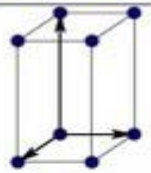
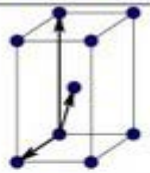
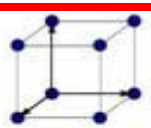
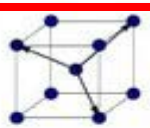
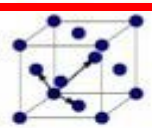
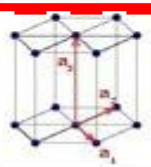
The 7 Crystal Systems

The **Bravais lattices** are divided into **7 *crystal systems*** defined by: lengths a, b, c and angles α, β, γ between the primitive translation vectors and exhibit **different levels of symmetry**.

The resulting crystal systems are:

Crystal System	Lengths	Angles
cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$
trigonal	$a = b = c$	$\alpha = \beta = \gamma < 120^\circ, \neq 90^\circ$
hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$
tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
monoclinic	$a \neq b \neq c$	$\alpha = \beta = 90^\circ \neq \gamma$
triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma$

In **3D**, there are **14 distinct** **Bravais lattices**:

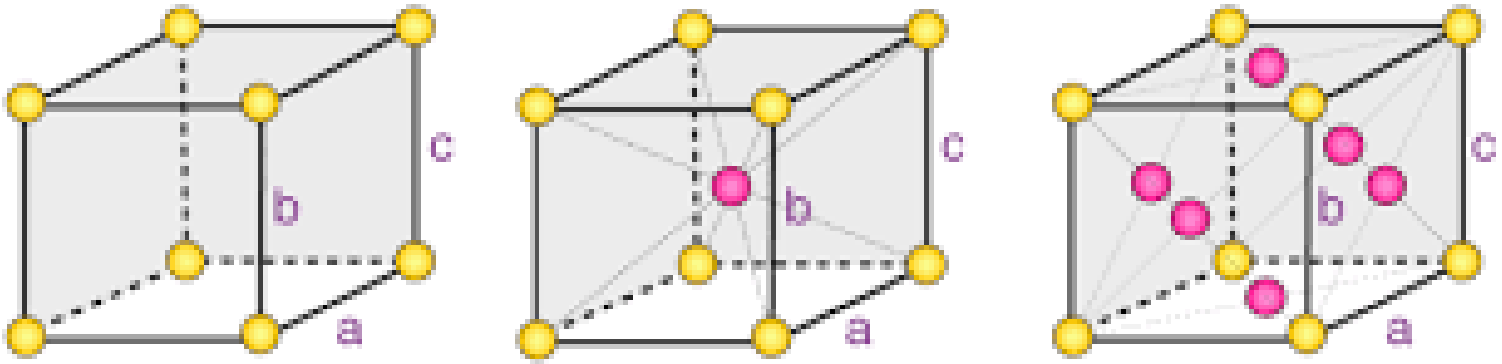
Bravais lattice	Parameters	Simple (P)	Volume centered (I)	Base centered (C)	Face centered (F)
Triclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} \neq \alpha_{23} \neq \alpha_{31}$				
Monoclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{23} = \alpha_{31} = 90°$ $\alpha_{12} \neq 90°$				
Orthorhombic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Tetragonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Trigonal	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} < 120°$				
Cubic	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Hexagonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = 120°$ $\alpha_{23} = \alpha_{31} = 90°$				

Most Semiconductors

Some Semiconductors

Sem

The **Cubic System** of Bravais lattices

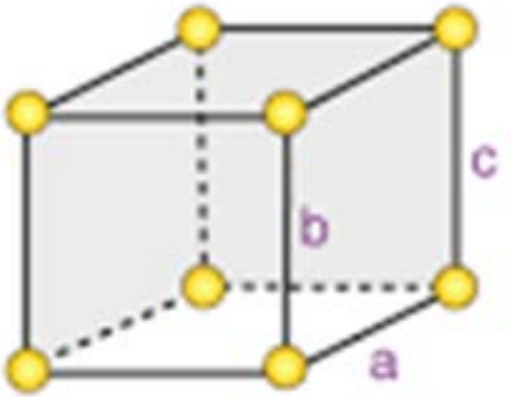


Simple cubic

Body-centred Cubic Unit Cell (BCC)

Face-centred Cubic Unit Cell (FCC)

Cubic Bravais lattices & primitive unit cells



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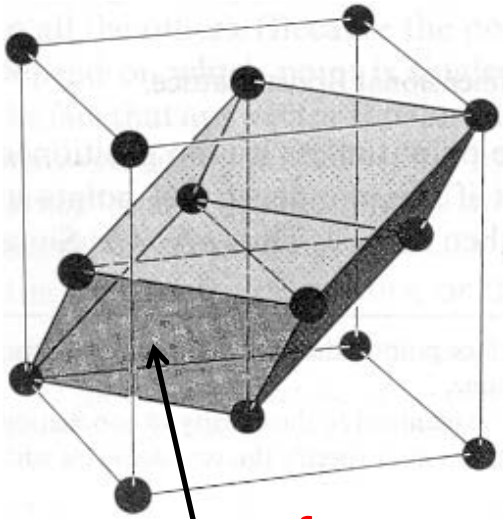
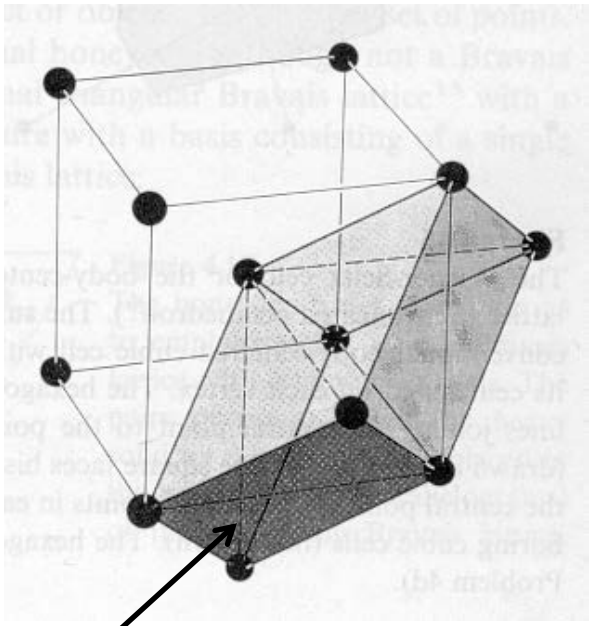
Primitive Unit Cell → Cubic



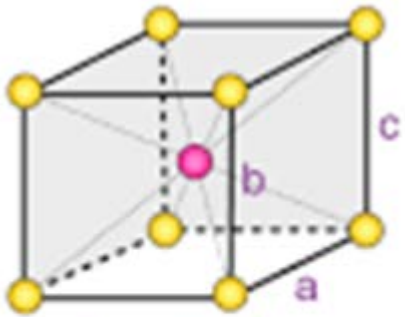
fcc



bcc

Primitive Unit Cell → Rombohedral

Cubic Bravais lattices: Lattice points & lattice vectors



Body-centred Cubic Unit Cell (BCC)

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

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

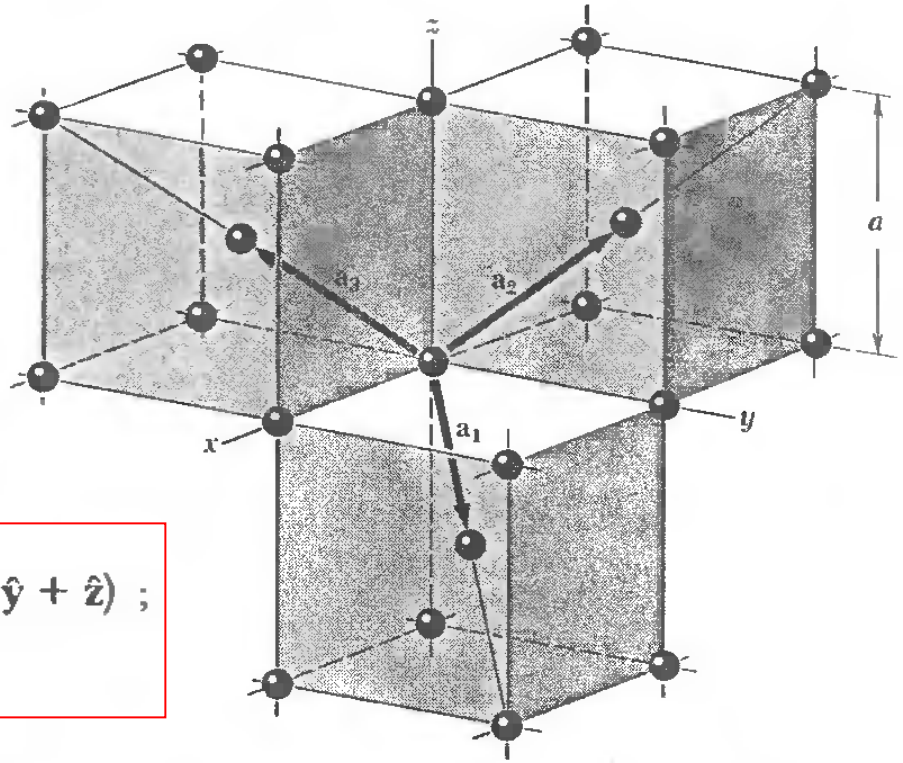
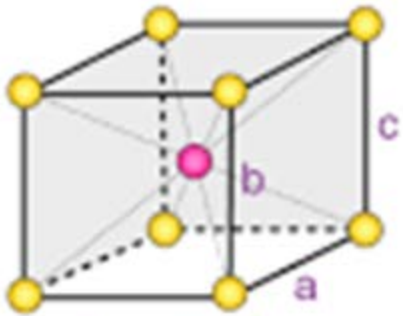


Figure 12 Primitive translation vectors of the body-centered cubic lattice; these vectors connect the lattice point at the origin to lattice points at the body centers. The primitive cell is obtained on completing the rhombohedron. In terms of the cube edge a the primitive translation vectors are

Cubic Bravais lattices: Lattice points & lattice vectors



Body-centred Cubic Unit Cell (BCC)

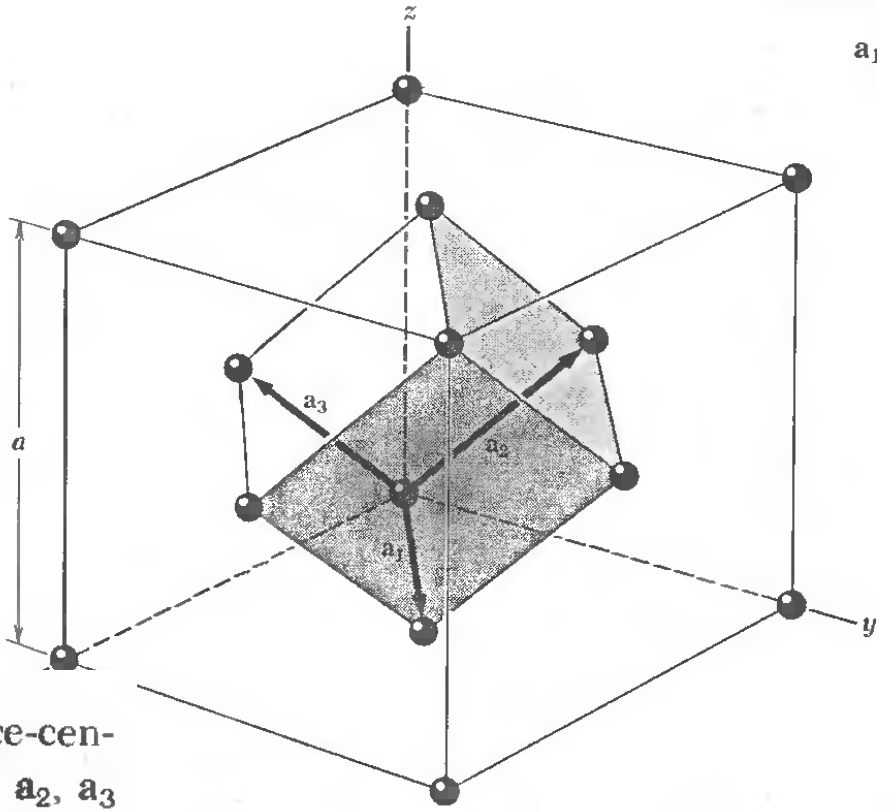
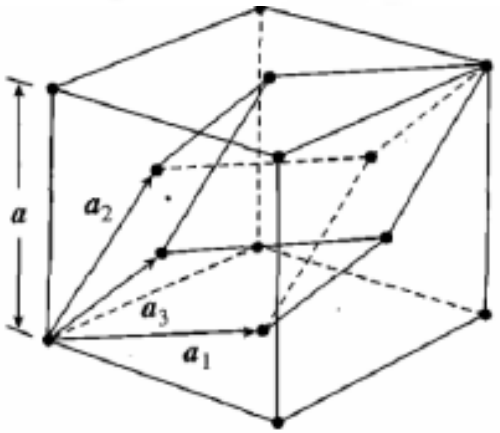


Figure 13 The rhombohedral primitive cell of the face-centered cubic crystal. The primitive translation vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ connect the lattice point at the origin with lattice points at the face centers. As drawn, the primitive vectors are:

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

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



Typical crystal structures

of

Elemental & Compound Semiconductors

Diamond lattice

coordination number = 4
tetrahedral coordination

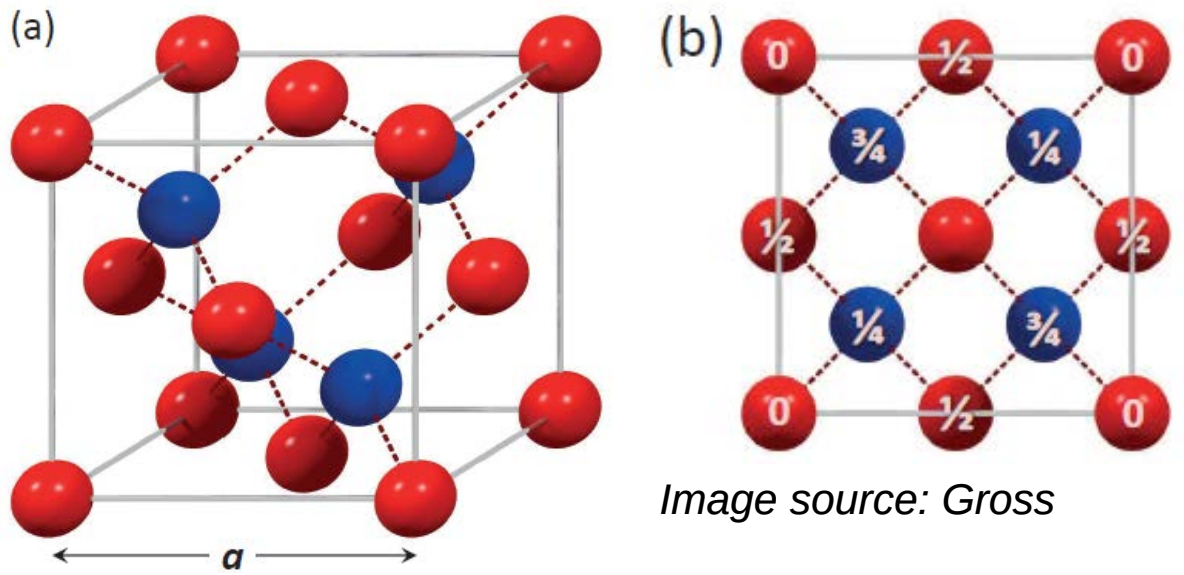


Image source: Gross

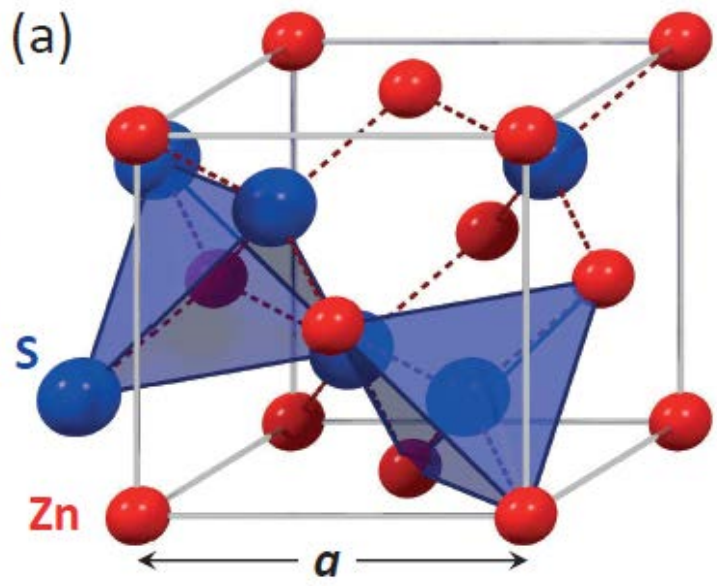
crystal	a (Å)
C(diamond)	3.57
Si	5.43
Ge	5.66
α-Sn	6.49

- two interpenetrating fcc sublattices one displaced from the other by ¼ of the distance along the diagonal of the cell ($a\sqrt{3}/4$);
- blue and red balls: represent the two non-equivalent (but identical) atoms of the basis;
- two different atoms in the basis: **zincblende lattice** (*e.g.* GaAs).

Compound Semiconductors crystal structure

Zincblende lattice (cubic structure)

coordination number = 4
tetrahedral coordination



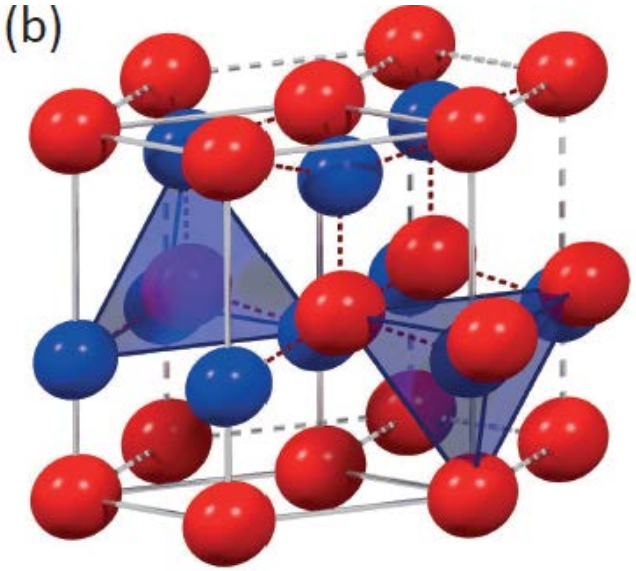
crystal	a (Å)
AlSb	6.13
GaP	5.45
GaAs	5.65
GaSb	6.12
InAs	6.04
InSb	6.48
SiC	4.35

- two interpenetrating fcc sublattices one displaced from the other by ¼ of the distance along the diagonal of the cell ($a\sqrt{3}/4$)
- blue and red balls: represent the two different atoms in the basis:

Compound Semiconductors crystal structure

Wurtzite lattice (hexagonal structure)

coordination number = 4
tetrahedral coordination



- Hexagonal space lattice with two sublattices per primitive cell
- blue and red balls: represent the two different atoms in the basis, e.g. red = S and blue = Zn in β-ZnS

Numerical characterisation of crystal structures

N = Nr. of lattice points per unit cell

$$N = Nb + Ne \cdot \frac{1}{Ue} + Nc \cdot \frac{1}{Uc}$$

Nb = Nr. of lattice points contained in the volume of the unit cell

Ne = Nr. of lattice points on the edges of the unit cell

Ue = Nr. of unit cells sharing one „edge“ lattice point

Nc = Nr. of lattice points at the corners of the unit cell

Uc = Nr. of unit cells sharing one lattice „corner“ lattice point

The **coordination number**, also called **ligancy,** of a central atom in a **molecule** or **crystal** is the number of atoms, molecules or ions bonded to it. This number is determined somewhat differently for molecules and for crystals:

- For molecules and polyatomic ions the coordination number of an atom is determined by simply counting the other atoms to which it is bonded (by either single or multiple bonds).

- The solid-state structures of crystals often have less clearly defined bonds, and in these cases a **count of neighboring atoms** is employed.

The **simplest method** is one used in **materials science**:

- The usual value of the coordination number for a given structure refers to an atom in the interior of a crystal lattice with neighbours in all directions.
  - the value for an interior atom is the **bulk coordination number;**
  - the value for an atom at a surface of the crystal is the **surface coordination number.**

In crystallography, **Atomic Packing Factor** (APF), **packing efficiency** or **packing fraction** is the fraction of volume in a crystal structure that is occupied by **constituent particles**.

It is a **dimensionless quantity** and **always less than unity**.

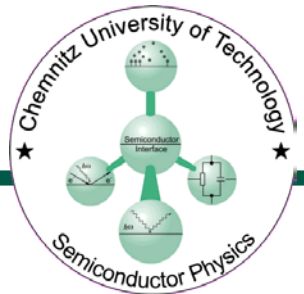
In atomic systems, by convention, the APF is determined by assuming that **atoms are rigid spheres**. The radius of the spheres is taken to be the maximal value such that the atoms do not overlap.

For one-component crystals (those that contain only one type of particle), the packing fraction is represented mathematically by:

$$\mathrm{APF} = \frac{N_{\mathrm{particle}} V_{\mathrm{particle}}}{V_{\mathrm{unit\ cell}}}$$

Basic Symmetry Elements of the Bravais cubic system

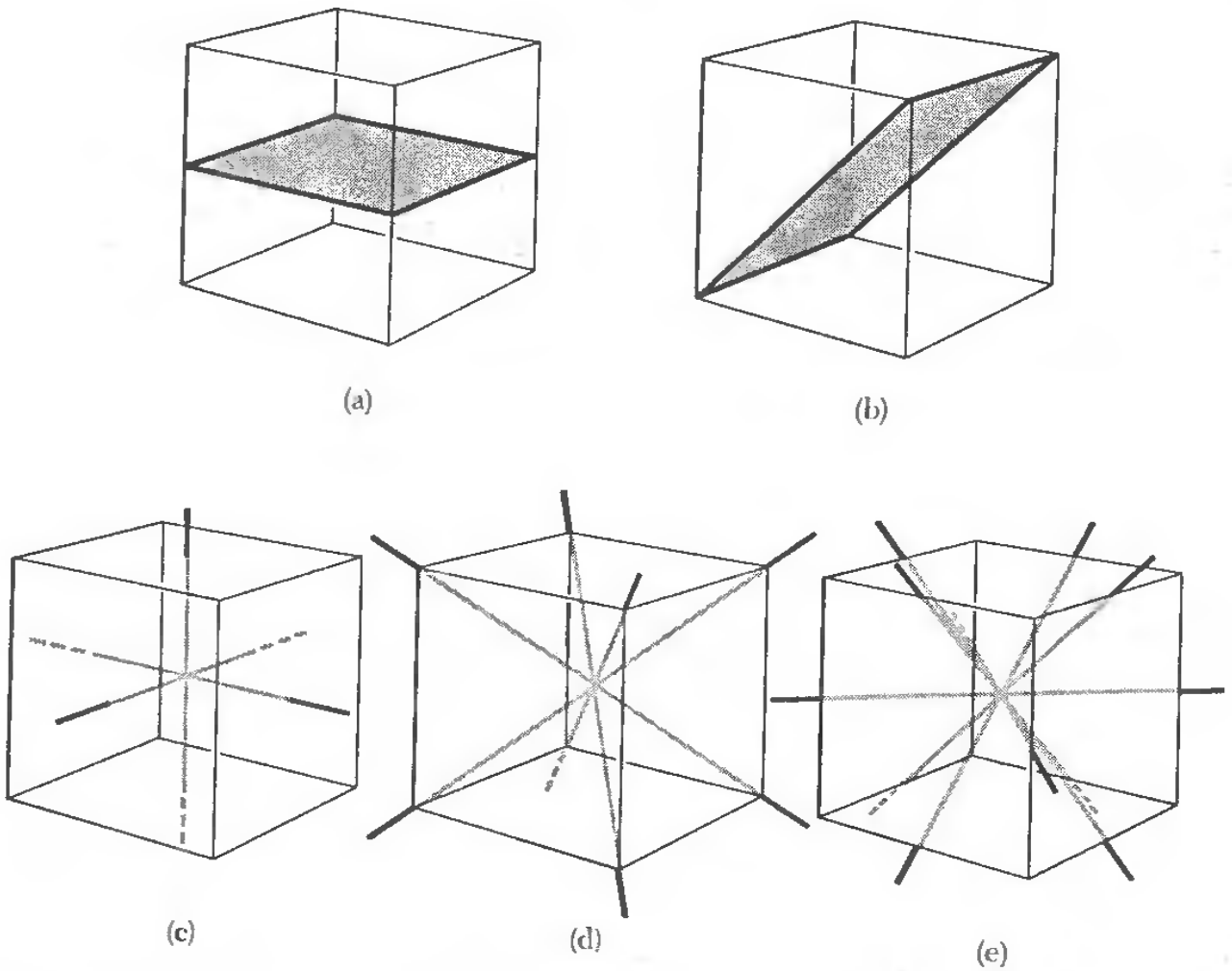
The Miller Indices



Symmetry Elements: planes, axis, points

CUBE

Most interesting for semiconductors

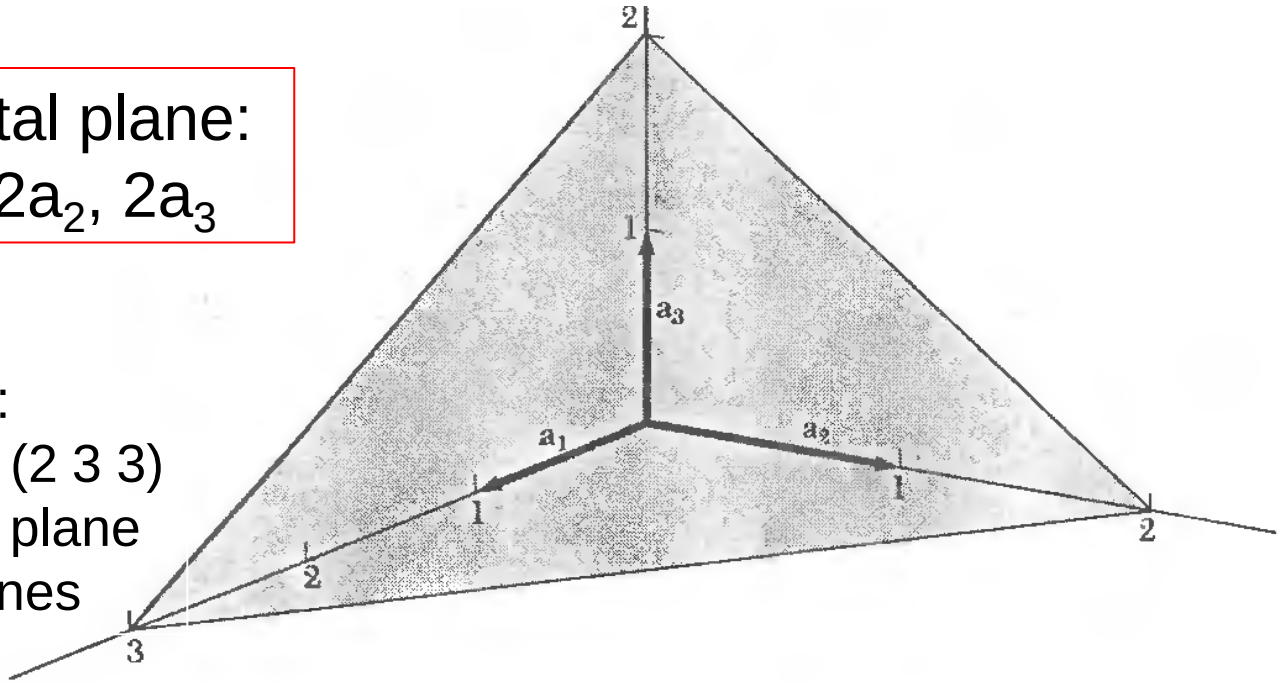


Crystal Planes and Directions

The **Miller indices** is the notation system in crystallography for planes in crystal (Bravais) lattices.

A **family of lattice planes** is determined by three integers ***h*, *k*, and *ℓ***, the ***Miller indices***.

Crystal plane:
$3a_1$, $2a_2$, $2a_3$



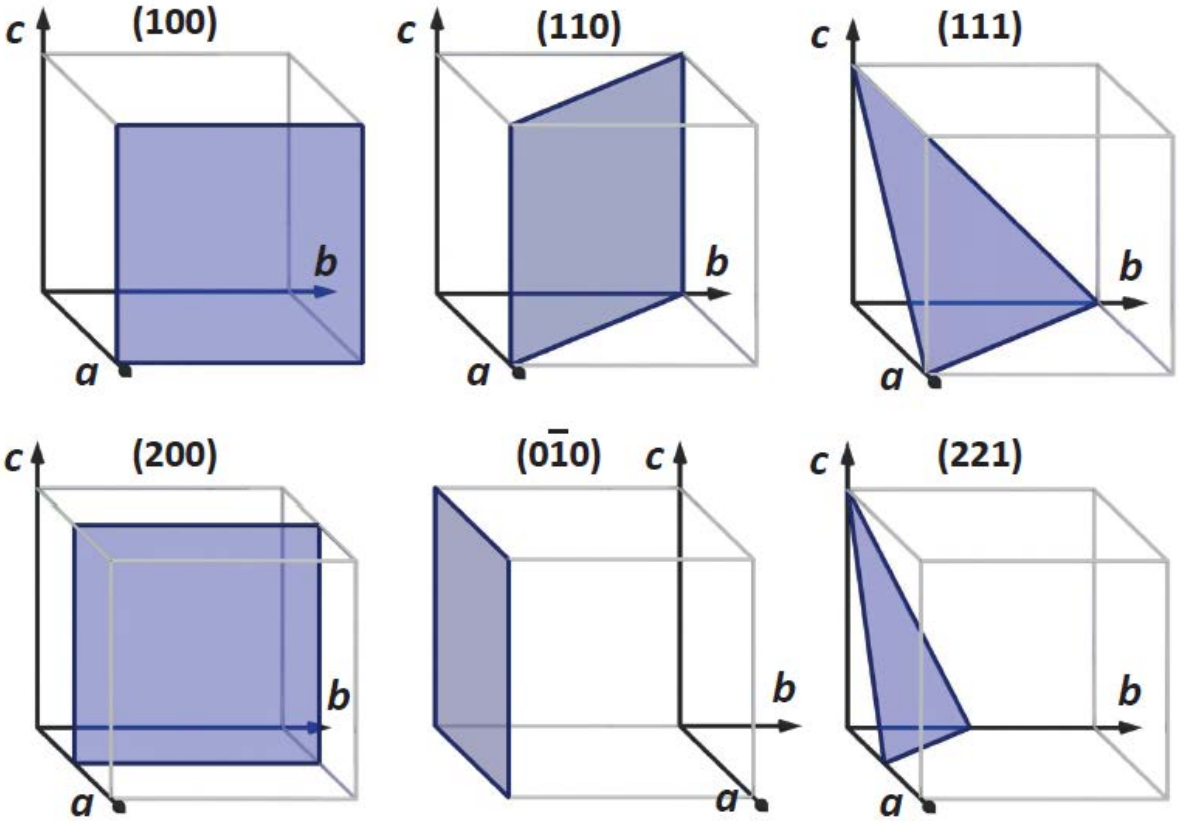
For structure analysis:
Miller indices (233) or (2 3 3)
- may denote a single plane
or a set of parallel planes

Figure 15 This plane intercepts the a_1, a_2, a_3 axes at $3a_1$, $2a_2$, $2a_3$. The reciprocals of these numbers are $\frac{1}{3}$, $\frac{1}{2}$, $\frac{1}{2}$. The smallest three integers having the same ratio are 2, 3, 3, and thus the indices of the plane are (233).

What is the procedure to determine the Miller indices?

(1) choose a plane not pass through (0, 0, 0)
(2) determine the intercepts of the plane with x, y, and z axes
(3) form the reciprocals of these intercepts
(4) find the smallest set of whole numbers that are in the same ratio as the intercepts

Crystal Planes and directions in the Bravais Cubic System



Planes: (*hkl*)
Family of planes: {*hkl*}
Directions: [*hkl*]

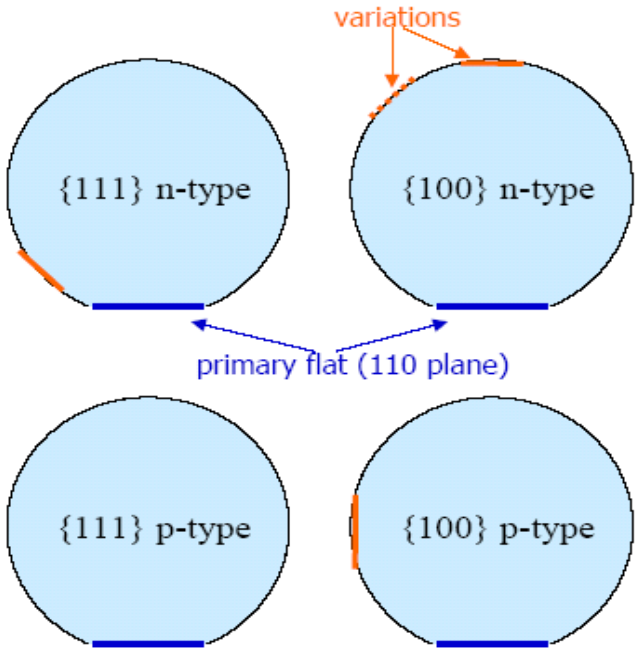
Distance between the (hkl) planes in the cubic system:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Wafer Identification

Doping

- n-type (e.g., Sb, As, P, Bi) electron donors (5 electrons in outer shell)
- p-type (e.g., B, Ga, In) acceptors (3 electrons in outer shell)



Note primary and secondary flats.

Orientation

Primary flat orientation

<111> p-type
<100> p-type
<111> n-type
<100> n-type

Secondary flat locations

no secondary flat
90° clockwise from primary flat
45° clockwise from primary flat
180° clockwise from primary flat

Typical crystal structures and latice parameters of some semiconductor materials.

Table 1.4 Lattice constants a in Å for representative cubic semiconductors at room temperature

Material	Structure	a	Ref.	Material	Structure	a	Ref
Si	diamond	5.43	a				
Ge	diamond	5.65	a	ZnS	zincblende	5.423	b
AlP	zincblende	5.431	b	ZnSe	zincblende	5.661	b
AlAs	zincblende	5.631	b	ZnTe	zincblende	6.082	b
AlSb	zincblende	6.142	b	CdS	zincblende	5.832	b
GaP	zincblende	5.447	b	CdSe	zincblende	6.052	b
GaAs	zincblende	5.646	b	CdTe	zincblende	6.423	b
GaSb	zincblende	6.130	b	PbS	rocksalt	5.935	b
InAs	zincblende	6.048	b	PbSe	rocksalt	6.152	b
InSb	zincblende	6.474	b	PbTe	rocksalt	6.353	b

a Kittel (1986)
b Weißmantel and Hamann (1979)

Next Lecture

THE RECIPROCAL SPACE & THE FOURIER TRANSFORM