Chapter 1 The Crystal Structure of Solids

→ Text deals primarily w/ semiconductors and their electrical properties. Most semiconductors are made of single-crystal materials.

Material types

1) Gasses/gases
2) Liquids
3) Solids → crystals are a subset.
4) Plasmas

→ Majority of materials used by electrical engineers for devices are solids.

1.1 Semiconductor Materials

From an electrical standpoint, materials can also be classified in terms of σ (S/m) or conductivity (i.e., how easily do the charge carriers pass through the material).

Conductors, $\sigma >> 1$ S/m, most metals

Superconductors $\sigma \to \infty$ → Typically low temp.

Insulators, $\sigma << 1$ S/m

Semiconductors, $\sigma \sim 1$ S/m between the above

1.1 cont.

* Semiconductor material can be single element, e.g., silicon (Si) and germanium (Ge), or they can be compounds, e.g., GaAs, InP, SiC, & GaN, that mostly are formed from combinations of group III & V elements as shown in Table 1.1 & Table 1.2.
* Due to $$$, semiconductor material research is very active.

1.2 Types of Solids

Solids are often broken down into 3 general types!

1) Amorphous – no order or very little order to arrangement of atoms

2) Polycrystalline – materials divided into ordered regions, called grains, divided by grain boundaries

3) Crystal / Single Crystal – material is essentially a single ordered region

see Figure 1.1

From *Semiconductor Physics and Devices: Basic Principles* (4th Edition), Donald A. Neamen, McGraw Hill, 2012, ISBN 978-0-07-352958-5.

Table 1.1 | A portion of the periodic table

III	IV	V
5 **B** Boron	6 **C** Carbon	
13 **Al** Aluminum	14 **Si** Silicon	15 **P** Phosphorus
31 **Ga** Gallium	32 **Ge** Germanium	33 **As** Arsenic
49 **In** Indium		51 **Sb** Antimony

Table 1.2 | A list of some semiconductor materials

Elemental semiconductors	
Si	Silicon
Ge	Germanium
Compound semiconductors	
AlP	Aluminum phosphide
AlAs	Aluminum arsenide
GaP	Gallium phosphide
GaAs	Gallium arsenide
InP	Indium phosphide

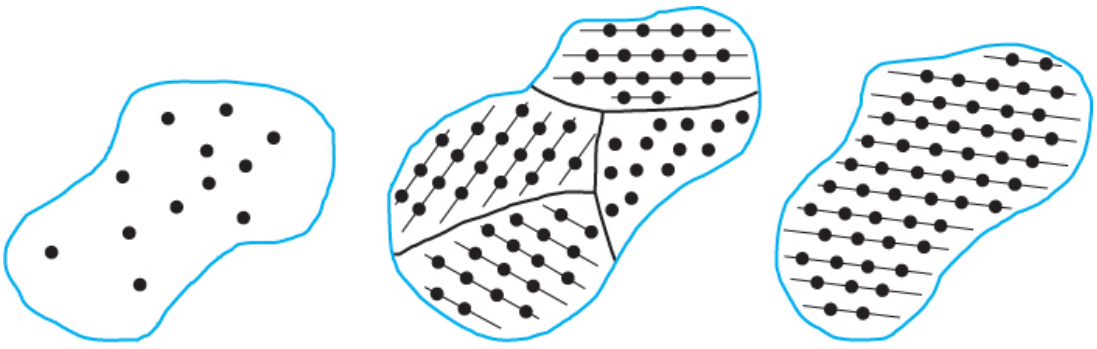


Figure 1.1 | Schematics of three general types of crystals: (a) amorphous, (b) polycrystalline, (c) single.

1.3 Space Lattices

Single-crystal materials are characterized by a repeating/periodic geometric arrangement of the atoms in the material, AKA *lattice*.

1.3.1 Primitive and Unit Cell

Unit Cell – small volume of the crystal that can be used to generate the entire crystal by cut-n-paste or translational repetition.

Primitive Cell – smallest unit cell that allows reproduction of crystal (not necessarily best for visualizing crystal)

→ Similar to period and fundamental period

For a three-dimensional crystal, every equivalent lattice point can be found using a position vector

$$\bar{r} = p\bar{a} + q\bar{b} + s\bar{c} \text{ (m)} \quad \text{(see Figure 1.4)}$$

where p, q, & s are integers, and $\bar{a}$, $\bar{b}$, & $\bar{c}$ are vectors (not necessarily orthogonal).

From *Semiconductor Physics and Devices: Basic Principles* (4th Edition), Donald A. Neamen, McGraw Hill, 2012, ISBN 978-0-07-352958-5.

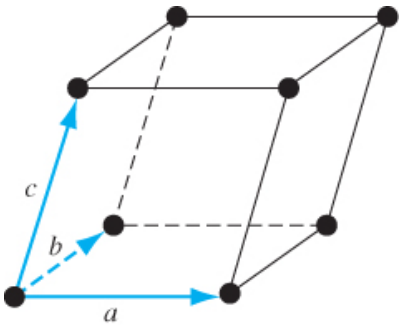


Figure 1.4 | A generalized primitive unit cell.

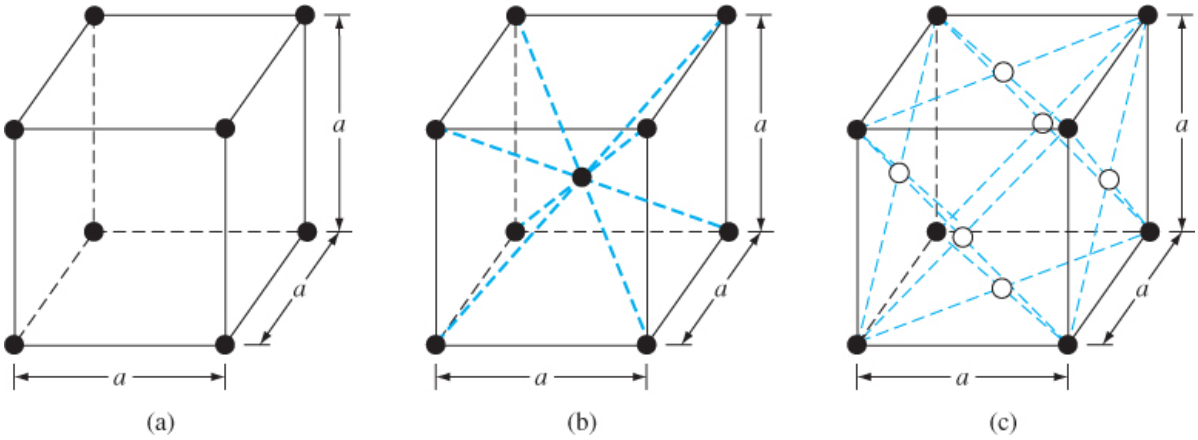


Figure 1.5 | Three lattice types: (a) simple cubic, (b) body-centered cubic, (c) face-centered cubic.

$\bar{a}$, $\bar{b}$, & $\bar{c}$ are lattice vectors (m)

a, b, & c are lengths of cell edges (m)

unit cell volume = $\bar{a} \cdot (\bar{b} \times \bar{c})$ (m^3)

1.3.2 Basic Crystal Structure

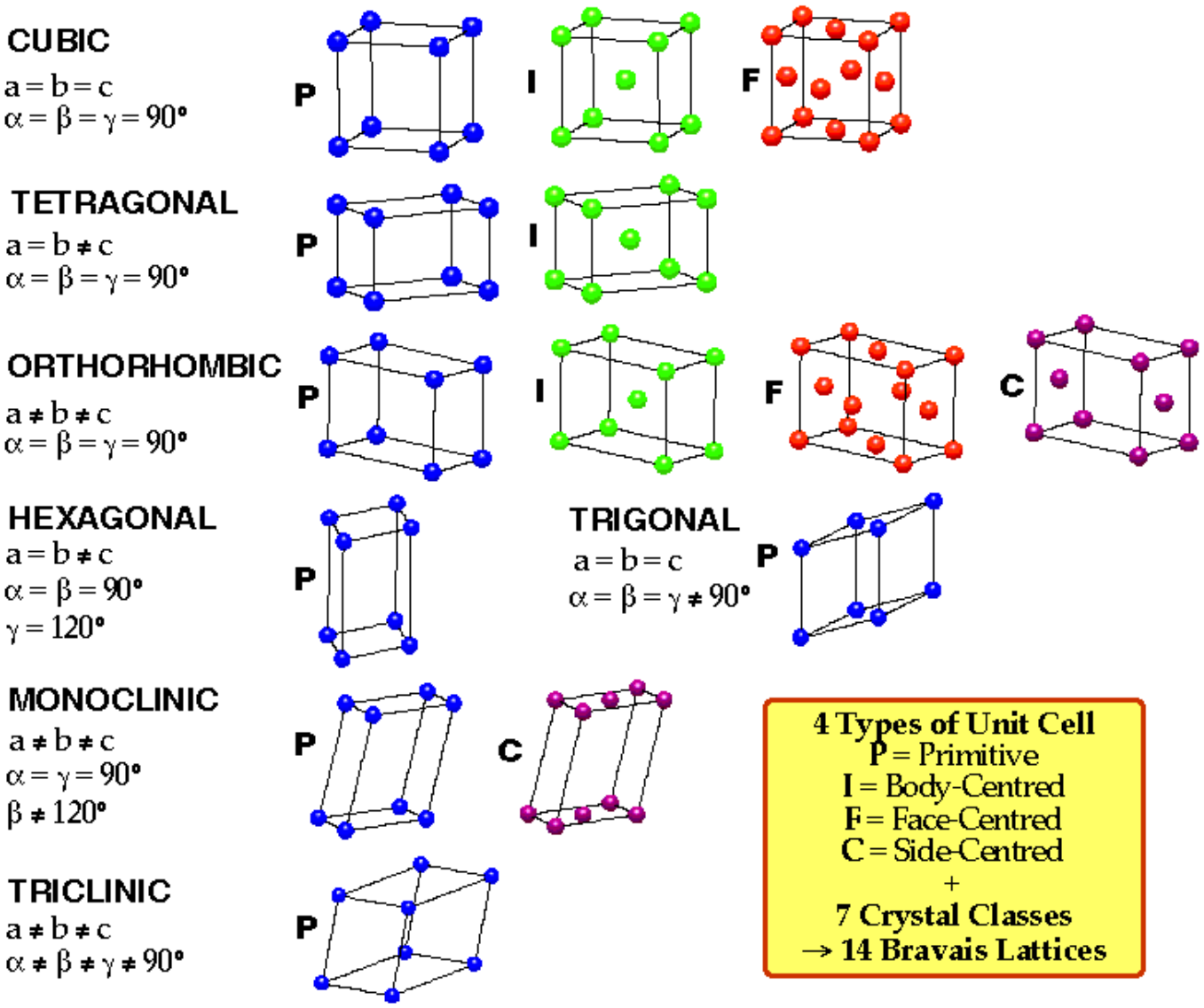
As shown in Figure 1.5, some unit cells have vectors $\bar{a}$, $\bar{b}$, & $\bar{c}$ that are both perpendicular/orthogonal and equal in length leading to cubic unit cells.

However, there are many more possibilities. In three dimensions, there are 14 different configurations called Bravais lattices (after the French physicist Auguste Bravais) determined by lattice systems and centering types

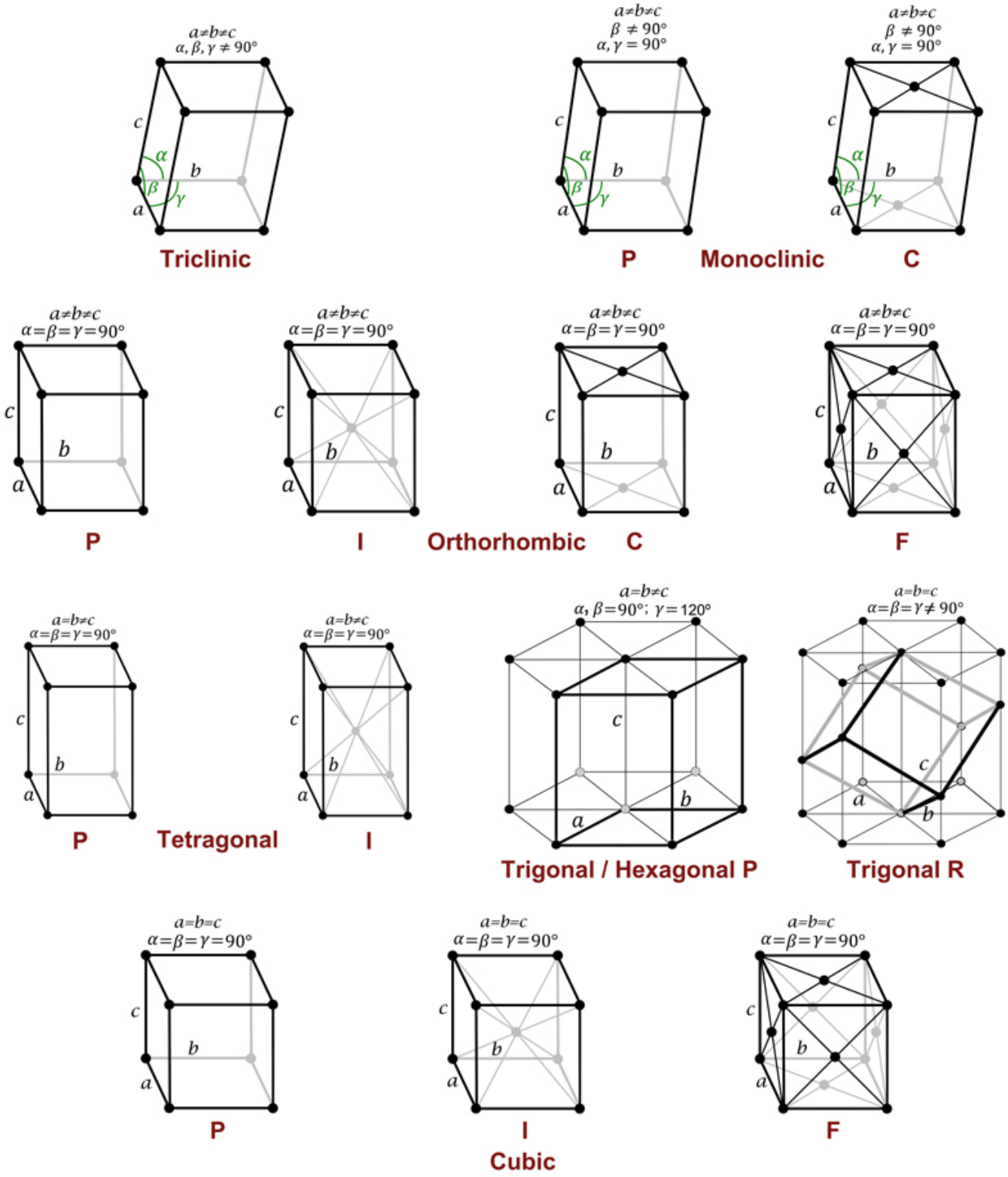
lattice systems	centering types
triclinic	primitive/simple
monoclinic	side-/base-/end-centered
orthorhombic	
tetragonal	body-centered
cubic	
rhombohedral	face-centered
hexagonal	

Bravais Lattices

From https://www.chm.bris.ac.uk/webprojects2003/cook/lattic1.gif

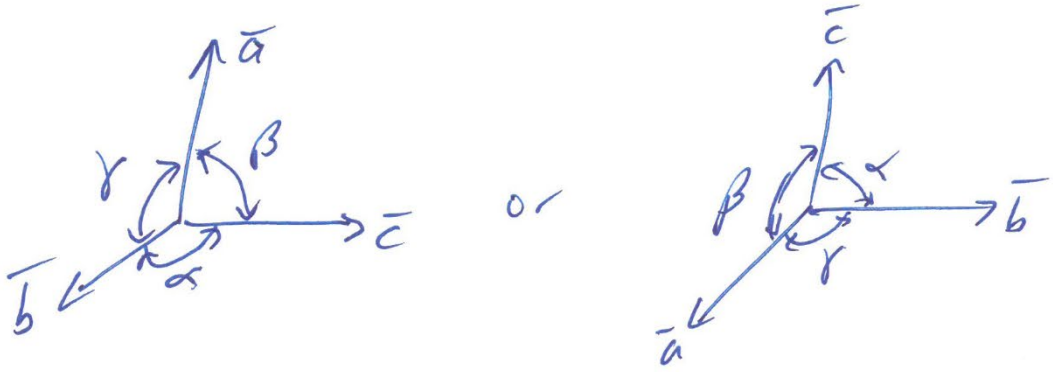


From https://www.xtal.iqfr.csic.es/Cristalografia/archivos_03/bravais-en.jpg



1.3.2 cont.

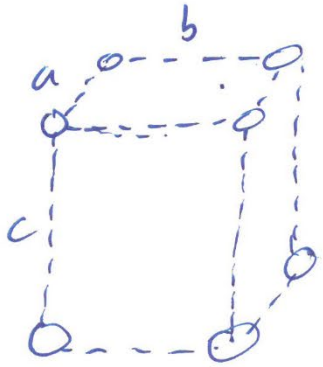
The angles α, β, and γ are opposite to the vectors $\bar{a}$, $\bar{b}$, and $\bar{c}$ respectively.



One parameter used to describe crystalline solids is the atomic volume density (a.v.d.)

$$\text{atomic vol. density} \equiv \frac{\#\text{ atoms per unit cell}}{\text{vol. of unit cell}}$$

ex.



$a = b = 6\ \text{Å} = 6 \times 10^{-10}\ \text{m}$

$c = 10\ \text{Å} = 10 \times 10^{-10}\ \text{m}$

Tetragonal (primitive/simple)

$$\#\text{ atoms per cell} = 8\left(\frac{1\ \text{octant}}{\text{atom}}\right) = 1$$

(# of atoms @ corners)

$$\text{a.v.d} = \frac{8(1/8)}{(6\times10^{-10})^2(10\times10^{-10})} = 2.7 \times 10^{27}\ \frac{\text{atoms}}{\text{m}^3}$$

1.3.3 Crystal Planes and Miller Indices

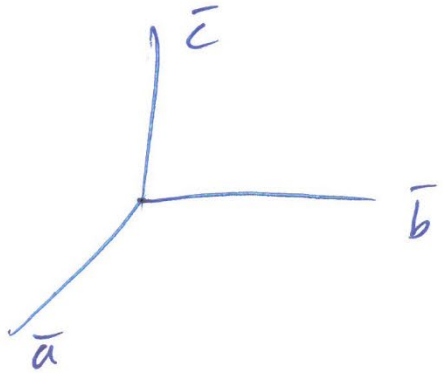
When working w/ semiconductors, devices (e.g., transistors) are typically fabricated at the surface. Therefore, we need a way to describe surface/planes and orientations for the crystalline materials.

Miller indices are the notation system used in crystallography to describe lattice planes.

We've already located lattice sites using

$$\bar{r} = p\,\bar{a} + q\,\bar{b} + s\,\bar{c}$$

where p, q, & s are integers.



Note: $\bar{a}$, $\bar{b}$, & $\bar{c}$ may/may not be orthogonal.

1.3.3 cont.

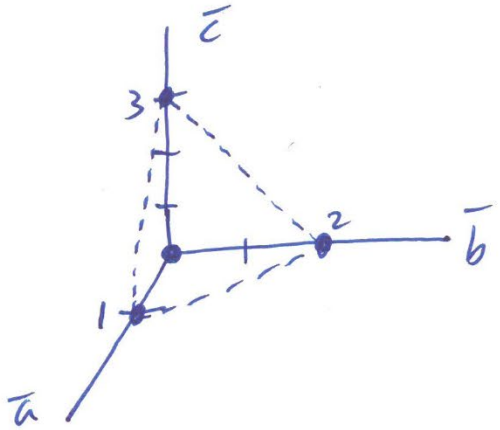
Find Miller indices (Method 1)

1) Find p, q, & s for the $\bar{a}$, $\bar{b}$, & $\bar{c}$ axis intercepts of the crystal plane for which we want indices.
   - → If plane does not have an intercept, set that integer to ∞.
   - → By convention, negative integers are written w/ a bar, e.g., $-3 \rightarrow \bar{3}$
   - → Avoid having intercept at origin! (Translate)
2) Invert each intercept and write the triplet $\left(\frac{1}{p}, \frac{1}{q}, \frac{1}{s}\right)$
3) Multiply the triplet by the lowest common denominator, i.e., the smallest integer needed to make each term in result an integer

   e.g., $(l.c.d.)\left(\frac{1}{p}, \frac{1}{q}, \frac{1}{s}\right) = (h, k, l)$
4) Drop the commas, & you have the Miller indices $(h\ k\ l)$

1.3.3 cont.

ex.



Find Miller indices for plane shown

1) $p = 1,\ q = 2,\ s = 3$

2) $\left(\frac{1}{1}, \frac{1}{2}, \frac{1}{3}\right)$

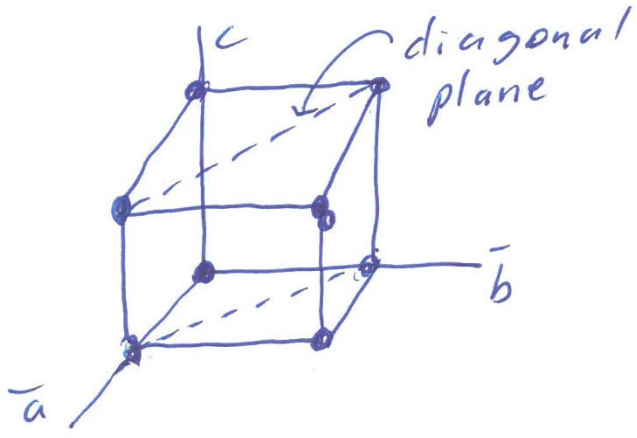
3) 6 is l.c.d.

$6\left(1, \frac{1}{2}, \frac{1}{3}\right) = (6, 3, 2)$

4) (6 3 2) is Miller index

$\Rightarrow$ This is the (6 3 2) plane.

ex. For the simple cubic lattice shown, find the Miller indices of the indicated plane



1) $p = 1,\ q = 1,\ c = \infty$

2) $\left(\frac{1}{1}, \frac{1}{1}, \frac{1}{\infty}\right) = (1, 1, 0)$

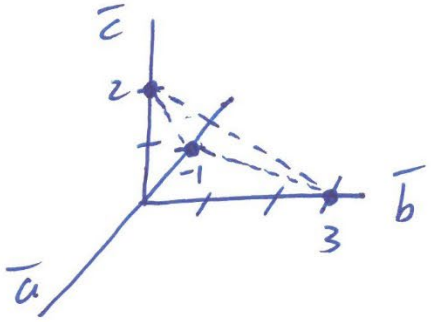
3) 1 is the l.c.d.

$1\,(1, 1, 0) = (1, 1, 0)$

4) This is the (1 1 0) plane.

1.3.3 cont.

ex.



Find Miller indices for plane indicated

1) $p=-1,\ q=3,\ s=2$

2) $\left(\frac{1}{-1}, \frac{1}{3}, \frac{1}{2}\right) = \left(\bar{1}, \frac{1}{3}, \frac{1}{2}\right)$

3) l.c.d. is 6

$6\left(\bar{1}, \frac{1}{3}, \frac{1}{2}\right) = (\bar{6}, 2, 3)$

4) This is the $(\bar{6}\ 2\ 3)$ plane.

Find Miller indices (Method 2)

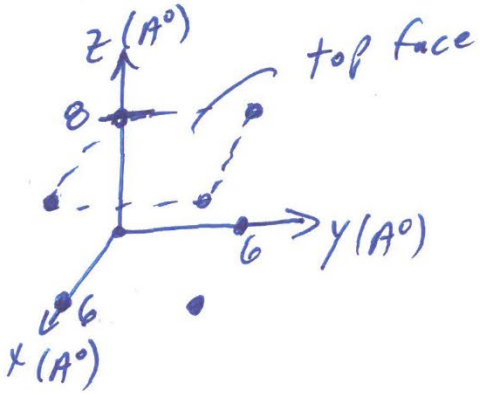
⇒ If $\bar{a}$, $\bar{b}$, & $\bar{c}$ are orthogonal, we can write $\bar{r}$ as $\bar{r} = pa\,\hat{a}_x + qa\,\hat{a}_y + sa\,\hat{a}_z$

or just designate the x-, y-, & z-intercepts as pa, qa, & sa where 'a' is some common factor

1) Find intercepts pa, qa, & sa
2) Invert each to form triplet $\left(\frac{1}{pa}, \frac{1}{qa}, \frac{1}{sa}\right)$
3) Find & multiply triplet by (l.c.d.)a
4) Drop commas to get Miller indices

1.3.3 cont.

ex.



1) x-intercept is ∞
y-intercept is ∞
z-intercept is 8 A°

2) $\left(\frac{1}{\infty}, \frac{1}{\infty}, \frac{1}{8A^\circ}\right)$

3) $(8A^\circ)\left(0, 0, \frac{1}{8A^\circ}\right) = (0, 0, 1)$

4) This is the (0 0 1) plane.

Related notations

→ {h k ℓ} denotes set of all planes that are equivalent to (h k ℓ) by symmetry of lattice.

e.g., all faces of a cubic lattice belong to {1 0 0}

1.3.4

→ [h k ℓ] denotes a direction (typically normal to a plane)

→ ⟨h k ℓ⟩ denotes set of all directions that are equivalent to [h k ℓ]

1.3.3 cont.

Other items of interest related to crystal planes are: 1) distance between parallel planes (straightforward geometry problem) and 2) atomic surface density (asd)

$$asd \equiv \frac{\#\text{ of atoms per lattice plane}}{\text{area of lattice plane}}$$

At this point, we'll also consider mass density and how we can calculate for crystals

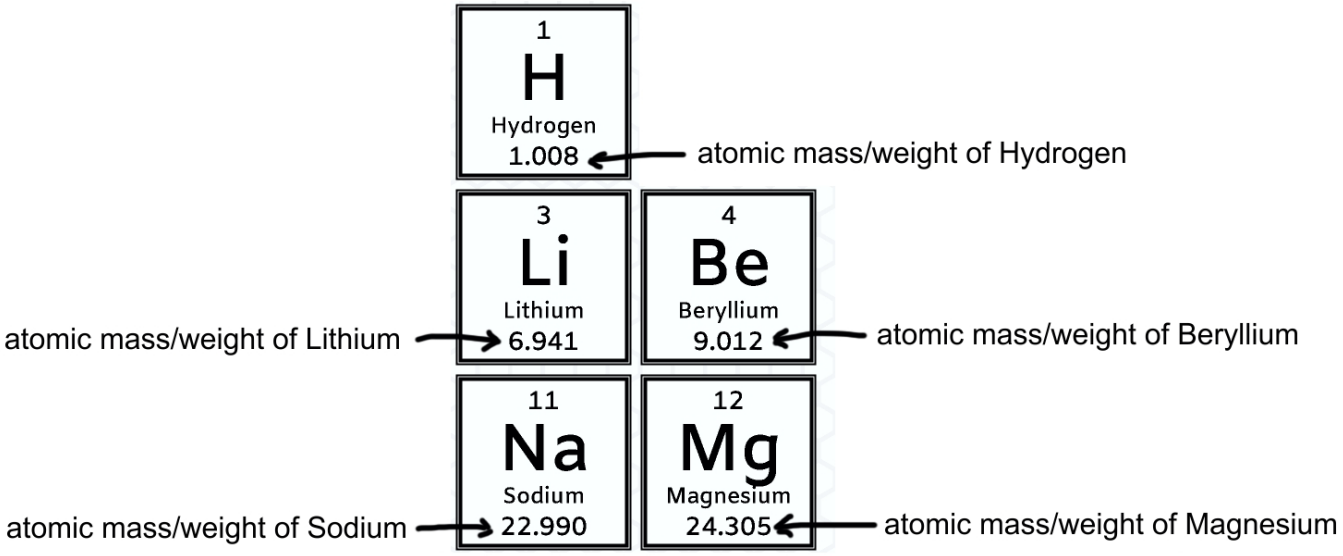
$$\text{mass density (md)} \equiv \frac{\text{mass of substance}}{\text{vol. containing substance}}$$

For crystals, let's consider

Avogadro's constant = $N_A = 6.02214 \times 10^{23}\ mol^{-1}$

where a mole (mol) is an aggregate of 6.02214×10^{23} elementary entities (i.e., atoms, molecules, ...)

Next, we have atomic weight or relative atomic mass A_r (see periodic table).



$$A_r = \frac{\text{average mass of atoms in sample}}{\text{atomic mass constant } (m_u)} \quad \left(\frac{g}{mol}\right)$$

$$m_u = \frac{\text{mass of carbon 12 atom}}{12}$$

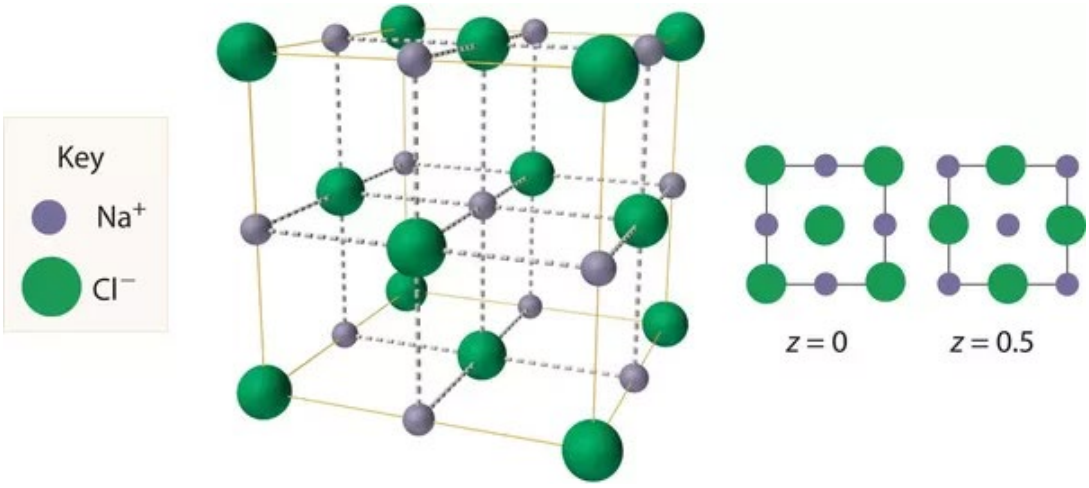
A_r takes into account that elements can have isotopes (e.g., carbon 13 versus carbon 12)

So, for crystals, we can find the mass density (m_d) by

$$m_d = \frac{av d_x (A_{r,x}) + av d_y (A_{r,y}) + \cdots}{N_A} \quad \frac{\left(\frac{\#}{m^3}\right)\left(\frac{g}{mol}\right)}{\left(\frac{\#}{mol}\right)} \Rightarrow \left(\frac{g}{m^3}\right)$$

Example- Calculate some quantities for sodium chloride/NaCl (AKA salt) crystal.

Per Wikipedia, sodium chloride (NaCl) has a face-centered cubic lattice/unit cell crystal structure (see below) with a lattice constant of 564 pm = 5.64 Å.



We can see that it can be broken into primitive cells with a simple cubic lattice with Na and Cl atoms occupying alternate corners with a lattice constant of 282 pm = 2.82 Å.

The atomic surface density (*asd*) of the top face of the cubic lattice would be:

$$asd_{top} = \frac{\#\text{ atoms on top}}{\text{area of top}} = \frac{4\,(0.25)}{\left(282*10^{-12}\right)^2}$$

$$\Rightarrow \quad \underline{\boldsymbol{asd_{top} = 1.2575 \times 10^{19}\ \text{atoms/m}^2 = 1.2575 \times 10^{15}\ \text{atoms/cm}^2}}.$$

The atomic volume density (*avd*) of the NaCl cubic lattice would be:

$$avd_{\text{NaCl}} = \frac{\#\text{ atoms in cell}}{\text{volume of cell}} = \frac{8\,(0.125)}{\left(282*10^{-12}\right)^3}$$

$$\Rightarrow \quad \underline{\boldsymbol{avd_{\text{NaCl}} = 4.459 \times 10^{28}\ \text{atoms/m}^3 = 4.459 \times 10^{22}\ \text{atoms/cm}^3}}.$$

The atomic volume density (*avd*) of the Na and Cl atoms would be:

$$avd_{\text{Na}} = avd_{\text{Cl}} = 0.5\, avd_{\text{NaCl}}$$

$$\Rightarrow \underline{\boldsymbol{avd_{\text{Na}} = avd_{\text{Cl}} = 2.23 \times 10^{28}\ \text{atoms/m}^3 = 2.23 \times 10^{22}\ \text{atoms/cm}^3}}.$$

To get the mass density (md_{NaCl}), we get the atomic mass for Na (22.99) and Cl (35.45) from the periodic table and use the atomic volume densities & Avogadro's constant N_A.

$$md_{\text{NaCl}} = \frac{avd_{\text{Na}}(\text{atomic weight of Na}) + avd_{\text{Cl}}(\text{atomic weight of Cl})}{N_A}$$

$$= \frac{2.23*10^{28}(22.99) + 2.23*10^{28}(35.45)}{6.02214*10^{23}}$$

$$\Rightarrow \quad \underline{\boldsymbol{md_{\text{NaCl}} = 2.16 \times 10^{6}\ \text{g/m}^3 = 2.16\ \text{g/cm}^3}}.$$

1.3.4 Directions in Crystals

As already mentioned, in terms of $\bar{r} = p\bar{a} + q\bar{b} + s\bar{c}$, we denote a direction as $[p\ q\ s]$

* for cubic lattices, the $[h\ k\ \ell]$ direction is orthogonal / perpendicular to the $(h\ k\ \ell)$ plane. This may/may not be true for other lattices.

1.4 The Diamond Structure

Why? Si & Ge have this structure

GaAs has a variation of this structure

In the diamond structure, each atom has 4 neighbors in a tetrahedral configuration / structure (see Fig 1.12) that is essentially a body-centered cubic w/ 4 corners removed. The overall structure can be thought of as two overlapping face-centered cubic lattices (Fig 1.11)

1.4 cont.

In a diamond structure, we have a single element. However, when a material w/ two elements takes on this configuration (e.g., GaAs), it is called a cubic sphalerite / sphalerite or zinchlende / zinc blende lattice.

(see Figs 1.14 & 1.15).

Examples of semiconductor lattices

[From Semiconductor Physics and Devices: Basic Principles (4th Edition), Donald A. Neamen, McGraw Hill, 2012, ISBN 978-0-07-352958-5.]

Both group IV semiconductors, **germanium or Ge** and **silicon or Si, have** unit cube/cell(s) as shown below. They consist of two sublattices, each face centered cubic (fcc) that overlap in a structure called a diamond lattice.

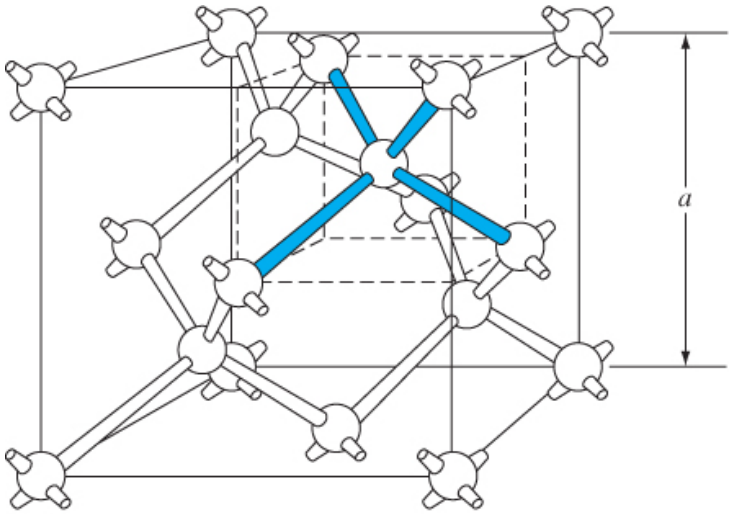


Figure 1.11 | The diamond structure.

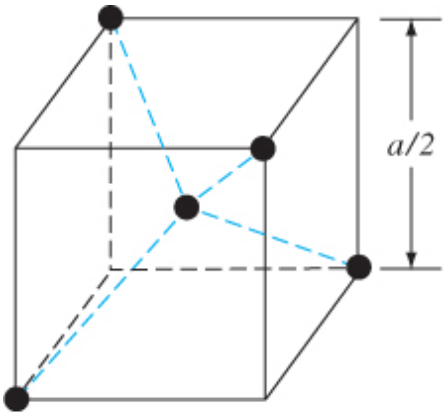


Figure 1.12 | The tetrahedral structure of closest neighbors in the diamond lattice.

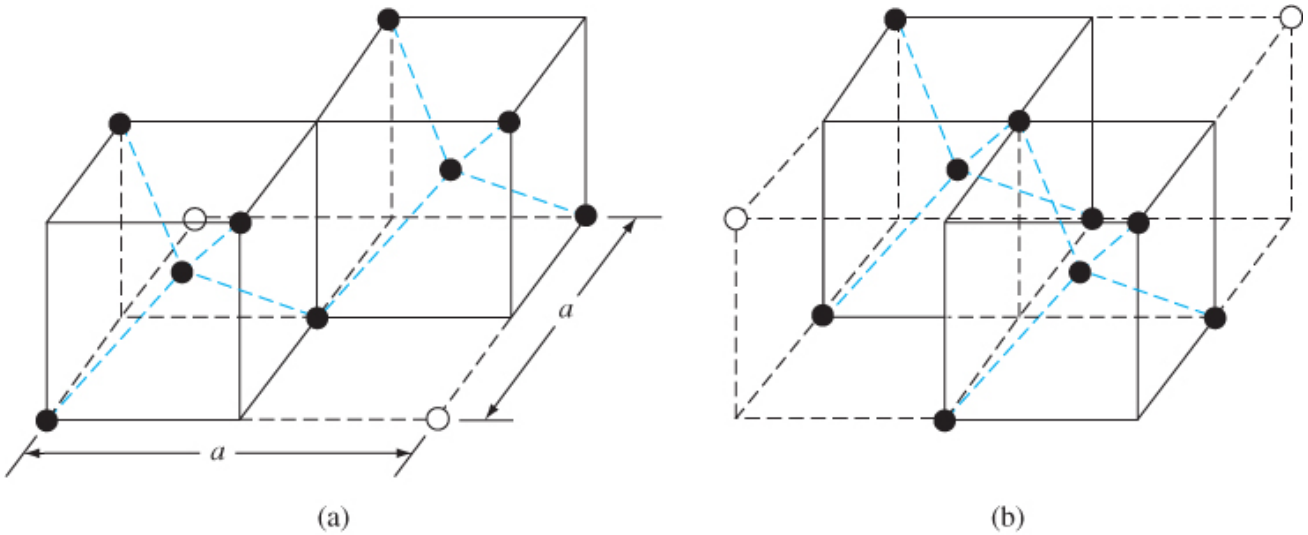


Figure 1.13 | Portions of the diamond lattice: (a) bottom half and (b) top half.

A **gallium arsenide or GaAs** unit cube/cell is shown below. It consists of two sublattices, each face centered cubic (fcc) and offset with respect to each other by half the diagonal of the fcc cube, a crystal configuration known as cubic sphalerite/sphalerite or zinc blende/zincblende. The key difference from the diamond lattice is that there are two different elements involved.

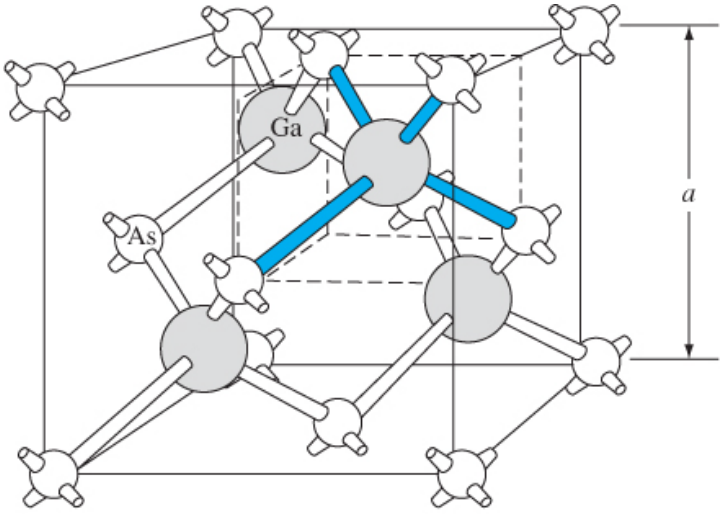


Figure 1.14 | The zincblende (sphalerite) lattice of GaAs.

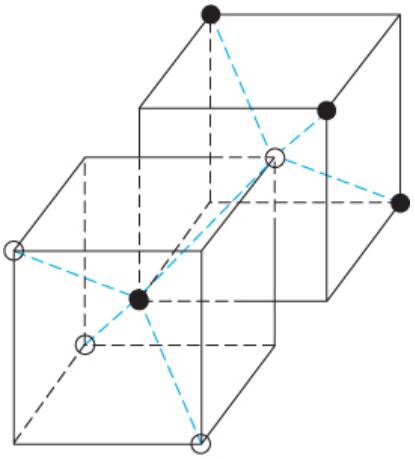


Figure 1.15 | The tetrahedral structure of closest neighbors in the zincblende lattice.

1.5 Atomic Bonding

Solids can be composed of atoms w/ 4 different atomic bonds:

1) Ionic Bonding
2) Covalent Bonding
3) Metallic Bonding
4) Van der Waals Bonding

Ionic

→ Typically occurs between atoms of elements on opposite sides of periodic table, e.g., NaCl, where one atom type (group I) loses an electron to become a positive ion while the other atom type (group VII) gains an electron to become a negative ion.

→ Usually the + and − ions alternate in the crystal lattice to achieve equilibrium

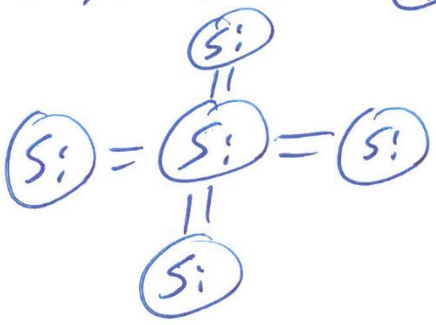
(+) (−) ← Coulomb attraction

1.5 cont.

Covalent

→ Here, the atoms in the material share electrons in the outer valence shells so that they can 'complete' or have closed-valence shells

ex. H_2 (hydrogen) H=H ← indicates covalent bond

ex. Si:  ← 4 neighbors

→ occurs w/ single element materials (group IV) or elements from middle groups of periodic table (e.g., group III + V)

Metallic

→ atoms are closely packed and typically the outermost electron shell of each overlaps w/ neighbors

→ essentially, bunch of + nuclei share a pool/sea of loosely bound electrons

1.5 cont.

Van der Waals

→ very weak bond (usually gases/liquids)

→ Usually these materials will only be solid @ very low temperatures

→ materials w/ weak electric dipoles that can attract one another

ex. HCl or HF form dipoles

→ Not of much interest to EEs and electronics

1.6 Imperfections and Impurities in Solids

→ In practice, materials/crystals are seldom perfect in structure and/or purity.

1.6.1 Imperfections in Solids

We'll focus on crystals.

1) lattice vibrations - spacing of atoms subject to change due to thermal, mechanical, ... energy causing lattice to vibrate. A reason why some electrical properties change w/ temperature.

2) point defects
   - → vacancy (atom missing from lattice)
   - → interstitial (atom located between lattice sites)
   - → vacancy-interstitial (both defects in close proximity, AKA Frenkel defect)

3) lattice defects

   e.g., line dislocation (lattice row terminates)

1.6.2 Impurities in Solids

→ Foreign atoms in material. Can be good (e.g., p & n doping of semiconductors) or bad/undesirable (e.g., oxygen in copper wires).

→ For crystalline materials, we can have:

1) Substitutional impurities where foreign atom(s) tables a normal lattice site.

2) Interstitial impurities where foreign atom(s) are located between normal lattice sites

Examples of Imperfections and Impurities in crystal lattices

From Semiconductor Physics and Devices: Basic Principles (4th Edition), Donald A. Neamen, McGraw Hill, 2012, ISBN 978-0-07-352958-5.

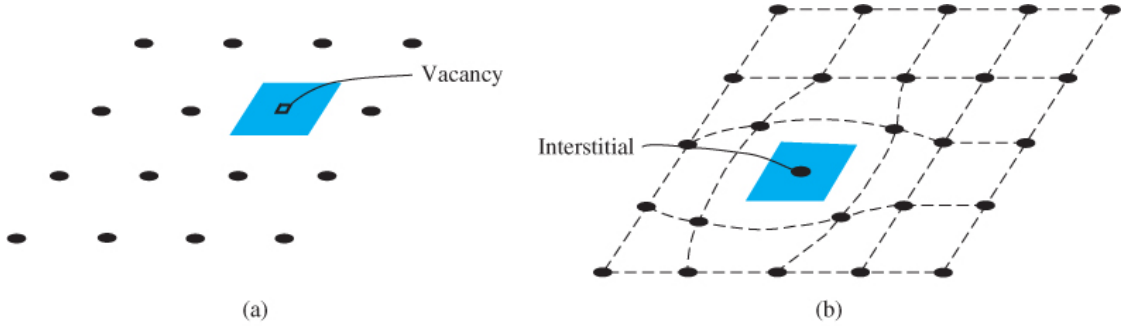


Figure 1.18 | Two-dimensional representation of a single-crystal lattice showing (a) a vacancy defect and (b) an interstitial defect.

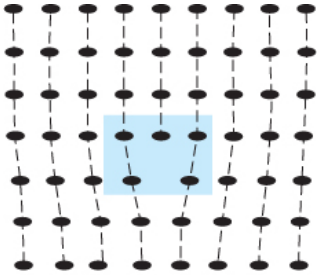
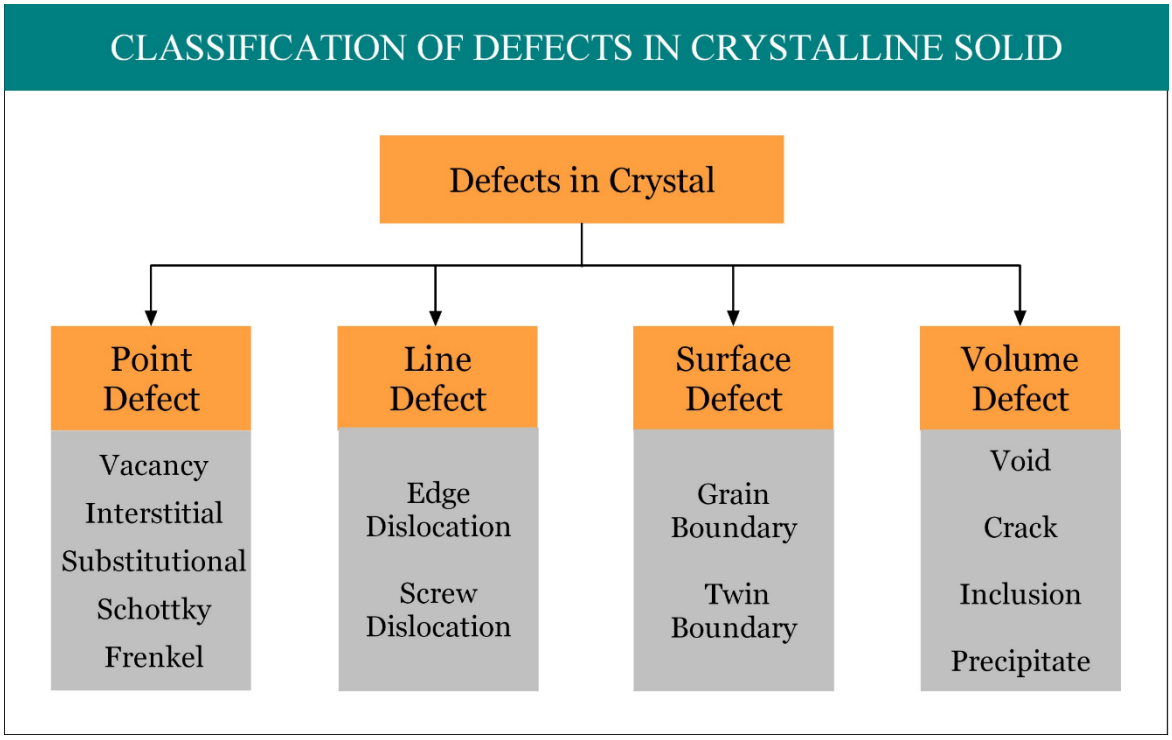


Figure 1.19 | A two-dimensional representation of a line dislocation.

https://www.minaprem.com/materials-science/defects/substitutional-defect-point-defect-defects-in-solid/



From Semiconductor Physics and Devices: Basic Principles (4th Edition), Donald A. Neamen, McGraw Hill, 2012, ISBN 978-0-07-352958-5.

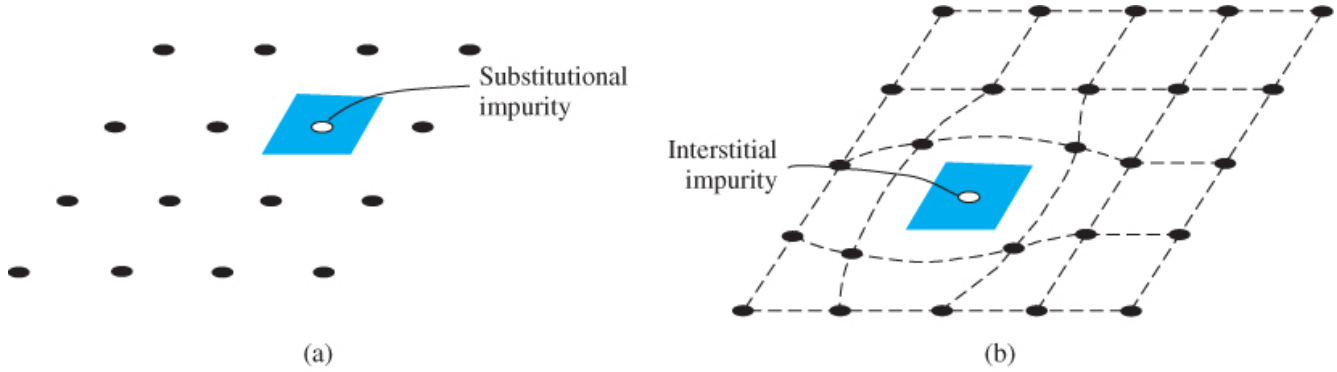


Figure 1.20 | Two-dimensional representation of a single-crystal lattice showing (a) a substitutional impurity and (b) an intersititial impurity.

From
https://www.substech.com/dokuwiki/doku.php?id=imperfections_of_crystal_structure