Materials Science

Lecture 9

Lebanese University - Faculty of Engineering – Branch 3

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Contents

Lecture 9:

Chap3: Crystalline Structure — Perfection

Exercises

Chap 3

Exercises

(part 3)

(a) Derive linear density expressions for FCC [100] and [111] directions in terms of the atomic radius R.

(a) Derive planar density expressions for FCC (100) and (111) planes in terms of the atomic radius R.

(b) Compute and compare planar density values for these same two planes for nickel.

The atomic radius for nickel is 0.125 nm

(a) Derive the planar density expression for the HCP (0001) plane in terms of the atomic radius R.

(b) Compute the planar density value for this same plane for magnesium.
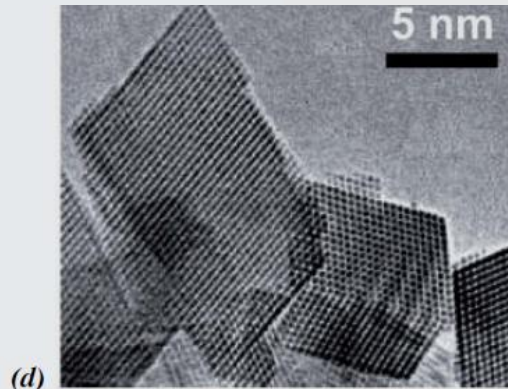
The atomic radius for magnesium is 0.160 nm

Contents

Example

(a) Schematic diagram showing the location of the catalytic converter in an automobile's exhaust system.

(a)

(b) Schematic diagram of a catalytic converter.

Stainless Steel Body

Insulation Packaging

Tail Pipe Emissions:
Water
Carbon Dioxide
Nitrogen

Catalyst Substrate

Exhaust Gases:
Hydrocarbons
Carbon Monoxide
Nitrogen Oxides

(b)

(c) Ceramic monolith on which the metallic catalyst substrate is deposited.

(c)

(d) High-resolution transmission electron micrograph that shows surface defects on single crystals of one material that is used in catalytic converters.

5 nm

(d)

Example

- Atomic **defects** are responsible for reductions of gas pollutant emissions from today's automobile engines.

- A **catalytic converter** is the pollutant-reducing device that is located in the automobile's **exhaust** system.

- Molecules of pollutant gases become **attached** to **surface defects** of **crystalline metallic materials** found in the catalytic converter. While attached to these sites, the molecules experience chemical reactions that convert them into other, non-polluting or less-polluting substances.
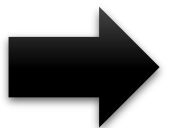
4.1. Introduction

Why study imperfections in solids?

◎ The **properties** of some materials are profoundly **influenced** by the **presence** of **imperfections**.

◎ Consequently, it is **important** to have a **knowledge** about the **types of imperfections** that exist and the roles they play in affecting the behavior of materials.

◎ **For example**, the **mechanical properties** of pure metals experience significant alterations when the metals are **alloyed** (i.e., when **impurity atoms are added**)— for example, **brass** (**70% copper/30% zinc**) is **much harder** and **stronger** than pure **copper**.

◎ Also, **integrated-circuit microelectronic** devices found in our **computers**, **calculators**, and home **appliances** function because of highly **controlled concentrations** of **specific impurities** that are incorporated into **small**, **localized regions** of **semiconducting** materials.

4.1. Introduction

Imperfection

◉ Thus far it has been tacitly assumed that **perfect order** exists throughout crystalline materials on an atomic scale. However, such an **idealized solid** **does not exist**; all contain **large numbers** of **various defects** or **imperfections**.

◉ As a matter of fact, many of the **properties** of materials are profoundly **sensitive** to **deviations from crystalline perfection**; the **influence is not always adverse**, and often specific characteristics are deliberately fashioned by the introduction of controlled amounts or numbers of particular defects.

◉ A crystalline **defect** refers to a **lattice irregularity** having one or more of its dimensions on the order of an atomic diameter.

◉ **Classification** of crystalline imperfections is frequently made **according to the geometry** or **dimensionality** of the defect; **point defects** (those associated with one or two atomic positions); **linear** (or one-dimensional) **defects**; **interfacial defects**, or boundaries, which are **two-dimensional,** and **Bulk or volume defects** which are **three-dimensional.**

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4.2. Vacancies And Self-interstitials

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Linear Defects
4.5. Dislocations—linear Defects

**Planar Defects**
4.6. Interfacial Defects

3D Imperfections

4.7. Bulk or Volume Defects

4.2. Vacancies And Self-interstitials

Vacancy

◉ The **simplest** of the point defects is a **vacancy**, or vacant lattice site, one normally occupied but from which an **atom is missing**.

◉ **All crystalline** solids **contain vacancies**, and, in fact, it is **not possible to create** such a material that is **free of these defects**.

◉ The necessity of the existence of vacancies is explained using principles of thermodynamics; in essence, the presence of vacancies **increases** the **entropy** (i.e., the **randomness**) of the crystal.
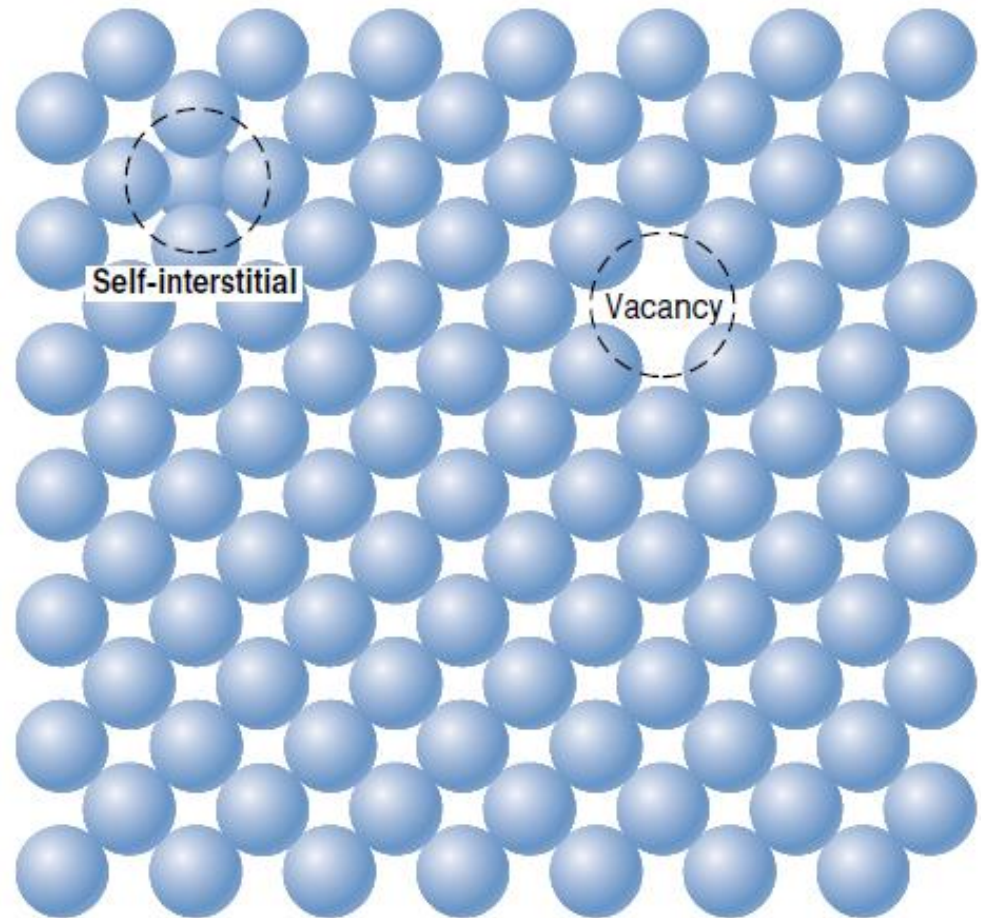
Two-dimensional representations of a vacancy and a self-interstitial.
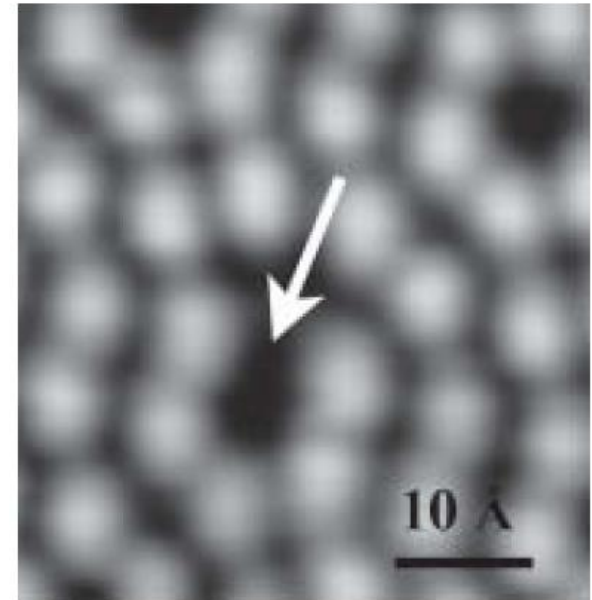
4.2. Vacancies And Self-interstitials

Vacancy

◉ The equilibrium number of vacancies N_v for a given quantity of material (usually per meter cubed) **depends on** and **increases** with **temperature** according to

$$N_v = N \exp\left(-\frac{Q_v}{kT}\right)$$

Scanning probe micrograph that shows a vacancy on a (111)-type surface plane for silicon. Approximately 7,000,000x.

N is the total number of atomic sites (most commonly per cubic meter), $\mathbf{Q_v}$ is the energy required for the formation of a vacancy (J/mol or eV/atom), **T** is the absolute temperature in kelvins, and **k** is the gas or **Boltzmann's constant**. The value of **k** is **1.38 x 10^{-23} J/atom.K**, or **8.62 x 10^{-5} eV/atom.K**, depending on the units of $\mathbf{Q_v}$.
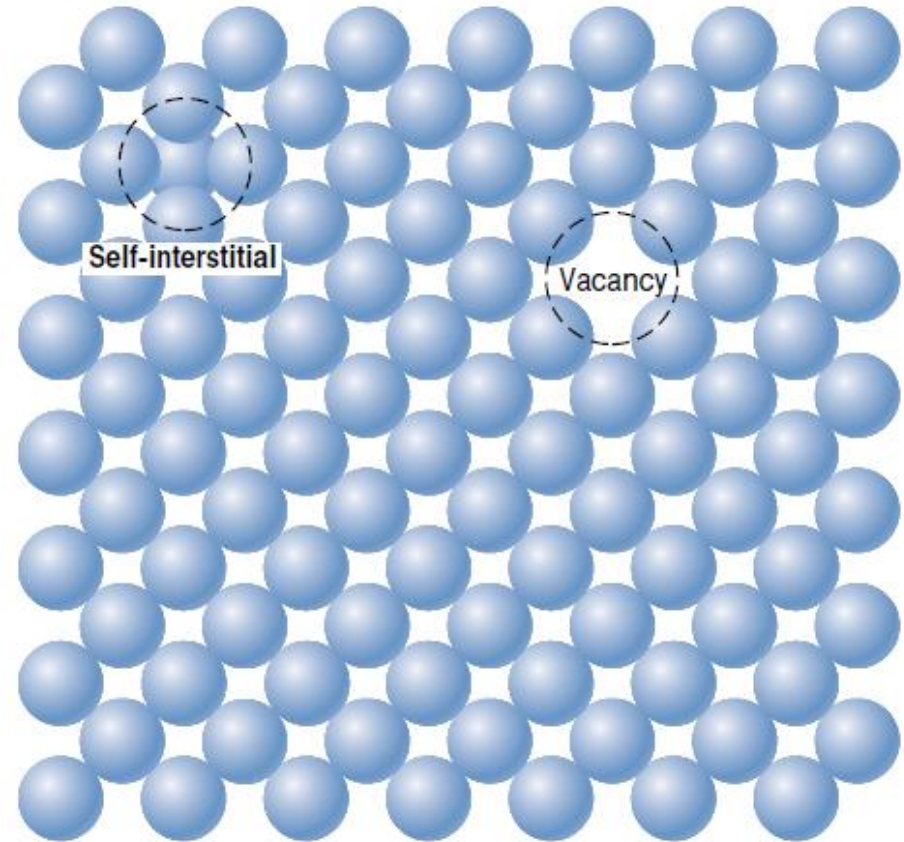
4.2. Vacancies And Self-interstitials

Vacancy

- Thus, the number of vacancies **increases exponentially with temperature**—that is, as **T increases**, so also does the term **exp(-Q_v/kT).**

- For most metals, the fraction of vacancies N_v/N just **below the melting temperature** is on the order of **10^{-4}**—that is, one lattice site out of **10,000** will be **empty**.

4.2. Vacancies And Self-interstitials

Self-interstitial

- A self-interstitial is an **atom** from the crystal that is **crowded** into an interstitial site—a small void space that under ordinary circumstances is not occupied.

- In metals, a self-interstitial introduces relatively **large distortions** in the **surrounding lattice** because the atom is **substantially larger** than the **interstitial position** in which it is situated.

- Consequently, the formation of this defect is **not highly probable**, and it exists in **very small concentrations** that are significantly **lower than** for **vacancies**.

Two-dimensional representations of a vacancy and a self-interstitial.

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Alloy

◉ A **pure metal** consisting of **only one type** of **atom** just **isn't possible**; **impurity** or foreign atoms are **always present**, and some exist as crystalline point defects.

◉ In fact, even with relatively **sophisticated techniques**, it is **difficult** to refine metals to a **purity** in excess of **99.9999%**. At this level, on the order of 10^{22} **to** 10^{23} **impurity atoms** are present **in 1 m^3** of material.

◉ Most **familiar metals** are **not** highly **pure**; rather, they are **alloys**, in which **impurity** atoms have been added intentionally to **impart specific characteristics** to the material.

◉ Ordinarily, **alloying** is used in metals to **improve mechanical strength** and **corrosion resistance**.

◉ **For example**, **sterling silver** is a **92.5% silver/7.5% copper alloy**. In normal ambient environments, **pure silver** is **highly corrosion resistant**, but also **very soft**. **Alloying with copper** significantly enhances the **mechanical strength** without depreciating the corrosion resistance appreciably.

Alloy

◉ The **addition of impurity atoms** to a metal results in the **formation** of a **solid solution and/or** a **new second phase**, depending on the kinds of impurity, their concentrations, and the temperature of the alloy.

◉ Several **terms** relating to impurities and solid solutions deserve mention. With regard to alloys, **solute** and **solvent** are terms that are commonly employed. **Solvent** is the element or compound that is present in the **greatest amount**; on occasion, solvent atoms are also called **host atoms**. **Solute** is used to denote an element or compound present in a **minor concentration**.

◉ A solid solution forms when, as the **solute atoms are added** to the **host material**, the **crystal structure is maintained** and **no new structures are formed**.

◉ Perhaps it is useful to draw an **analogy** with a **liquid solution**. If two liquids that are soluble in each other (such as **water and alcohol**) are combined, a **liquid solution** is produced as the **molecules intermix**, and its composition is **homogeneous** throughout.

◉ A **solid solution** is also **compositionally homogeneous**; the **impurity atoms** are randomly and uniformly **dispersed** within the solid.

Alloy

⦿ **Impurity point defects** are found in solid solutions, of which there are **two types**: **substitutional** and **interstitial**.

⦿ For the **substitutional** type, **solute or impurity atoms replace or substitute for the host atoms.**
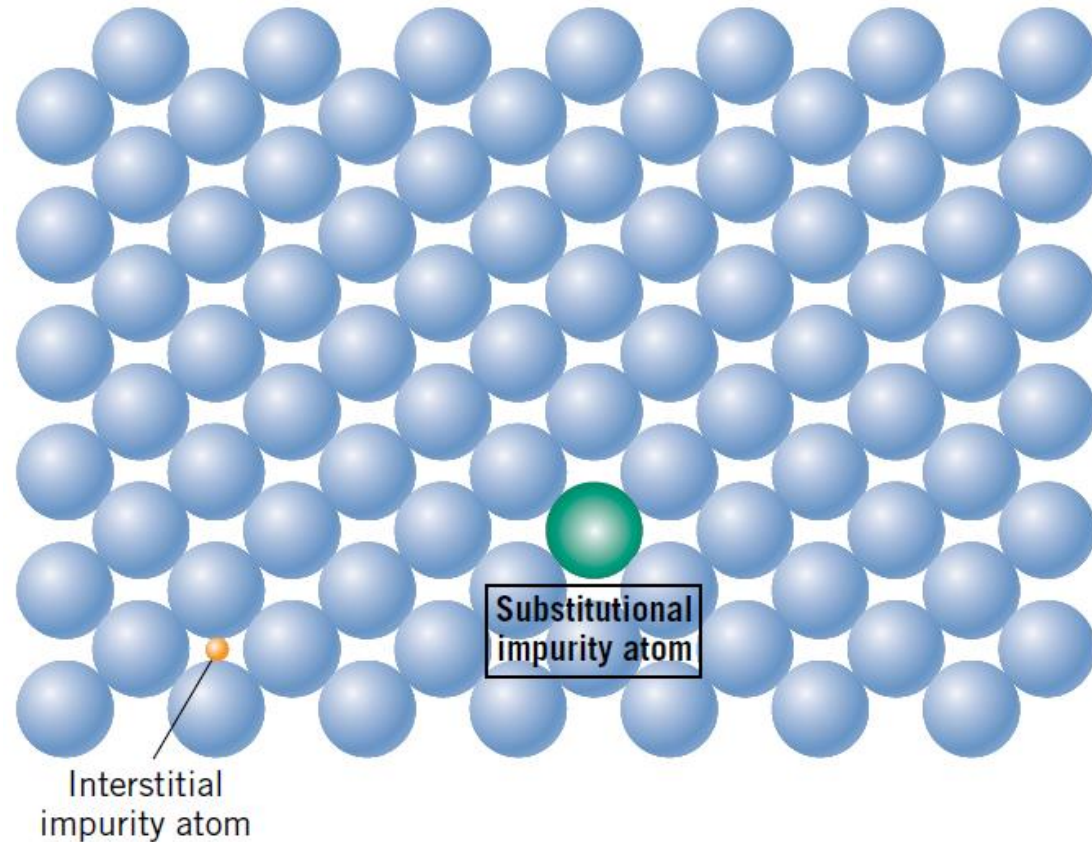
Substitutional impurity atom

Interstitial impurity atom

Two-dimensional schematic representations of substitutional and interstitial impurity atoms.

Substitutional solid solution

⦿ **Several features** of the solute and solvent atoms **determine** the **degree** to which the former dissolves in the latter. These are expressed as **four Hume–Rothery rules**, as follows:

1. **Atomic size factor.** Appreciable quantities of a solute may be accommodated in this type of solid solution only when the **difference** in **atomic radii** between the two atom types is less than about **±15%**. **Otherwise**, the solute atoms create **substantial lattice distortions** and a **new phase** forms.

2. **Crystal structure.** For **appreciable** solid solubility, the crystal structures for metals of both atom types **must be the same**.

3. **Electronegativity factor.** The **more electropositive one element** and the **more electronegative the other**, the greater the likelihood that they will form an **intermetallic compound instead** of a **substitutional solid solution**.

4. **Valences.** Other factors being equal, a metal has **more of a tendency** to **dissolve another** metal **of higher valency** than to dissolve one of a lower valency.
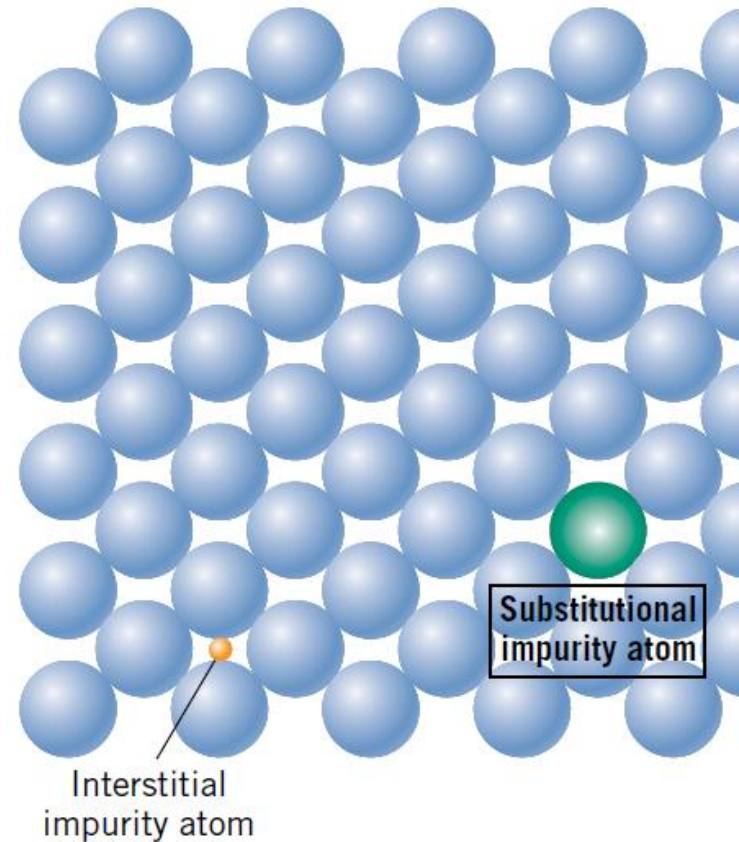
Substitutional solid solution

- **An example** of a substitutional solid solution is found for **copper and nickel**. These two elements are **completely soluble** in one another at **all proportions**. With regard to the aforementioned rules that govern degree of solubility, the **atomic radii** for copper and nickel are **0.128 and 0.125 nm**, respectively; **both** have the **FCC** crystal structure; and their **electronegativities** are **1.9 and 1.8**. Finally, the most common **valences** are **+1 for copper** (although it sometimes can be 2) and **+2 for nickel.**

4.3. Impurities In Solids

Interstitial solid solution

◉ For interstitial solid solutions, impurity atoms **fill the voids** or interstices among the host atoms.

◉ For both **FCC** and **BCC crystal structures**, there are **two types of interstitial sites**—**tetrahedral** and **octahedral**—these are **distinguished** by the number of nearest neighbor host atoms—that is, the **coordination number**.

◉ **Tetrahedral** sites have a coordination number of **4**; straight lines drawn from the centers of the surrounding host atoms form a four-sided tetrahedron.

◉ However, for **octahedral** sites the **coordination number** is **6**; an octahedron is produced by **joining** these **six sphere centers**.

Two-dimensional schematic representations of substitutional and interstitial impurity atoms.
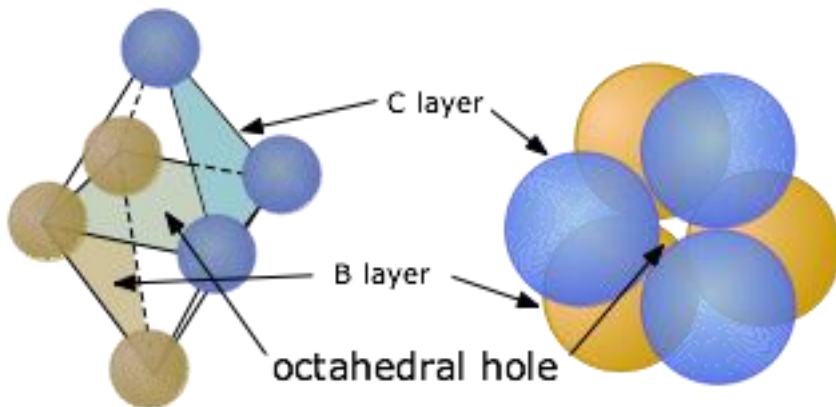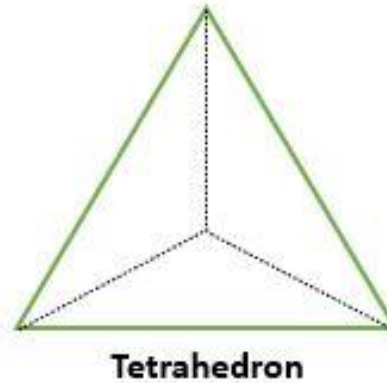
Interstitial solid solution

Interstitial solid solution

Tetrahedral Void

Tetrahedron

C layer

B layer
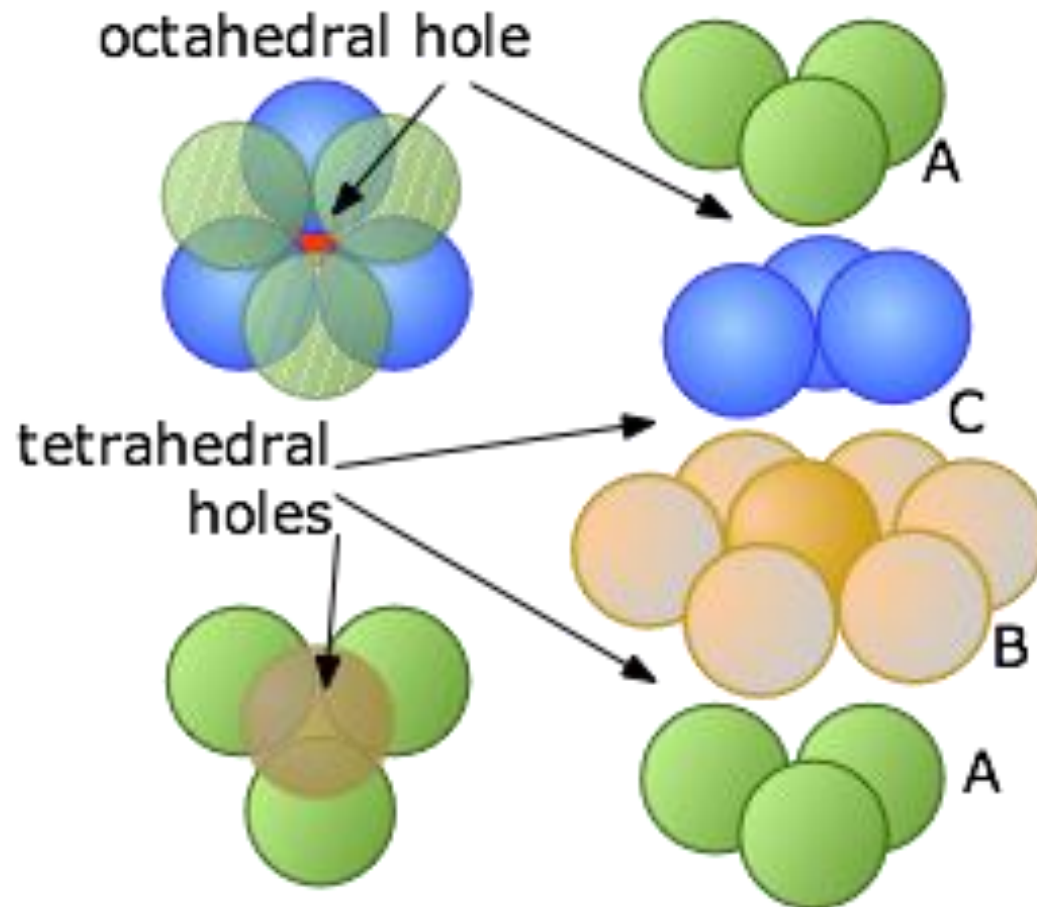
octahedral hole
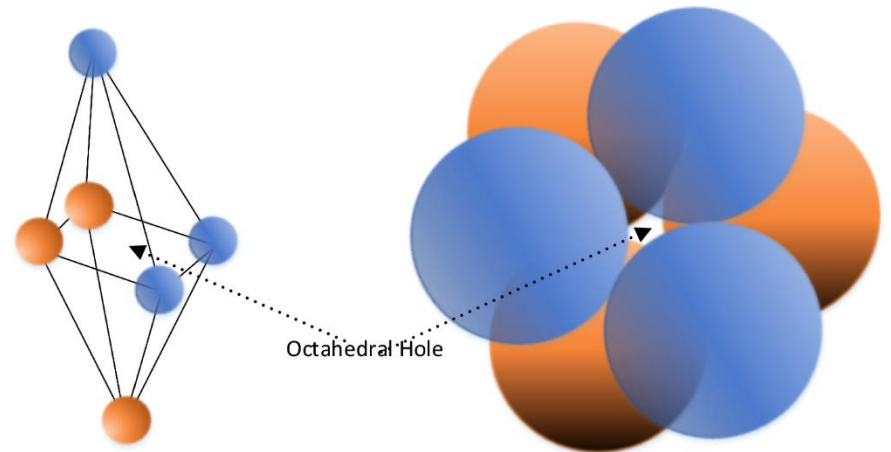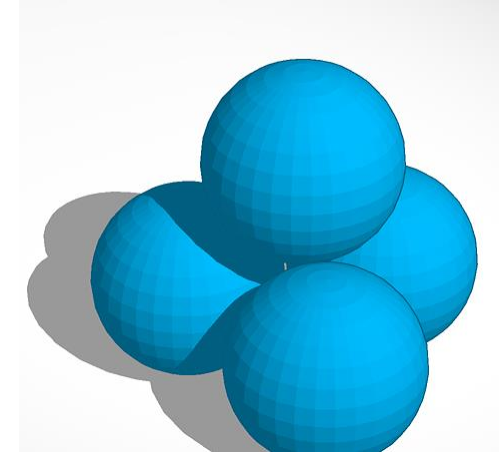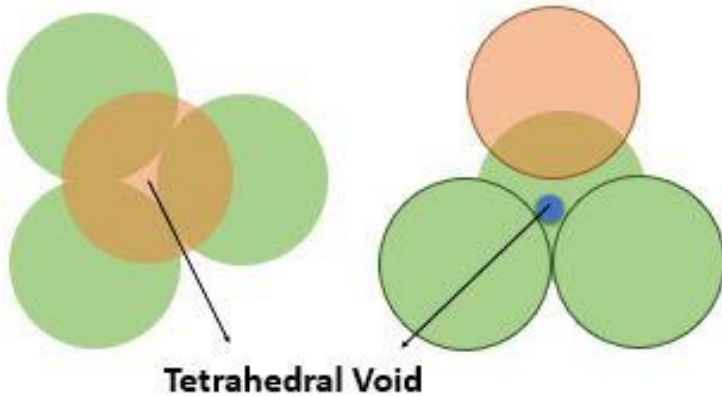
Octahedral Hole

4.3. Impurities In Solids

<u>Interstitial solid solution</u>

How can we define the locations of tetrahedral and octahedral interstitial sites ?
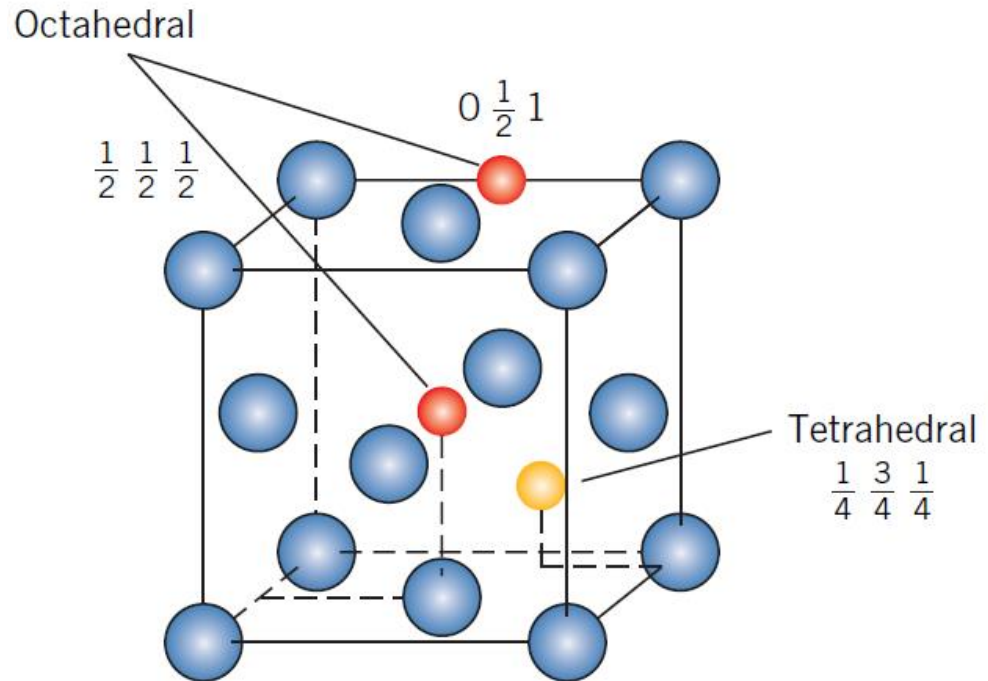
Watch the attached videos
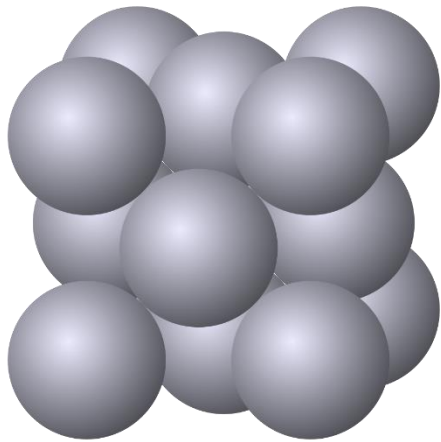
Interstitial solid solution

- For FCC, there are **two types** of **octahedral** sites with representative point coordinates of $0\ \dfrac{1}{2}\ 1$ and $\dfrac{1}{2}\dfrac{1}{2}\dfrac{1}{2}$.

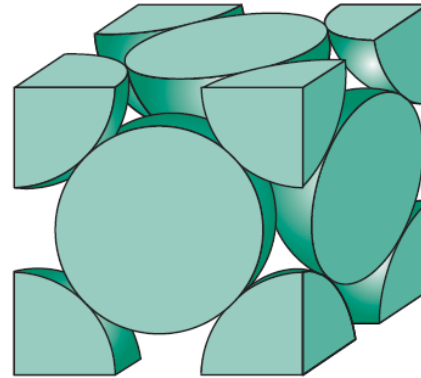- Representative coordinates for a single **tetrahedral** site type are $\dfrac{1}{4}\dfrac{3}{4}\dfrac{1}{4}$.

*Locations of tetrahedral and octahedral interstitial sites within **FCC** unit cell*

Interstitial solid solution
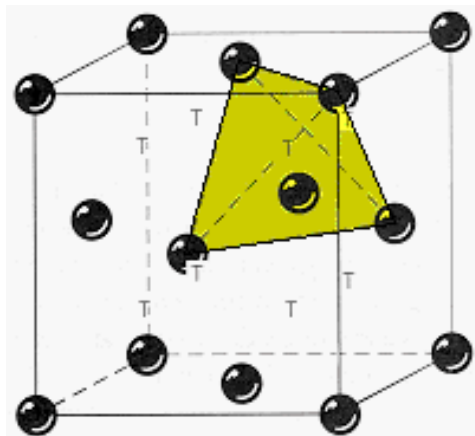
FCC crystal structure
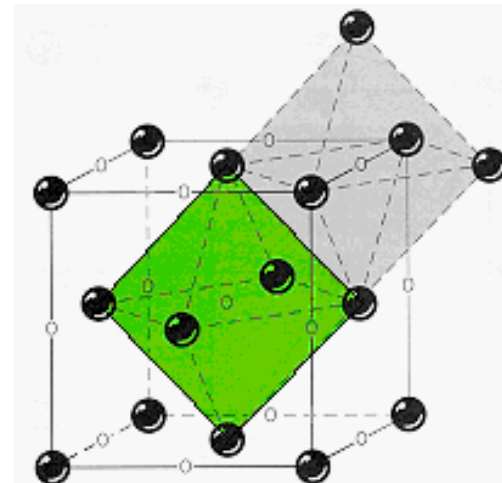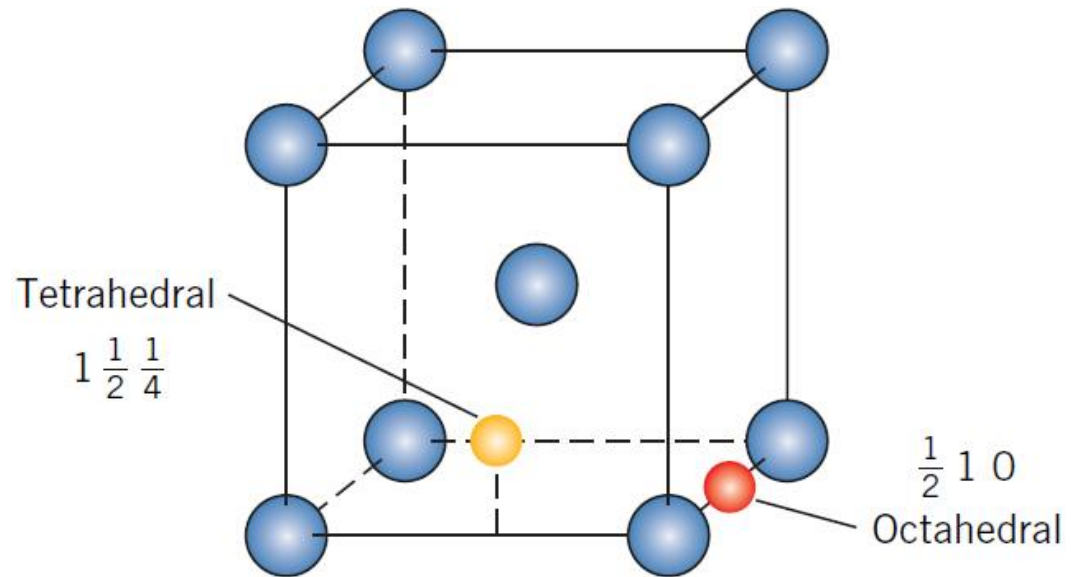
FCC unit cell

FCC tetrahedral voids

FCC octahedral voids

Interstitial solid solution

- **One type** of each of **octahedral** and **tetrahedral** interstitial sites is found for **BCC**.

- Representative coordinates are as follows: octahedral $\frac{1}{2}\,1\,0$ and tetrahedral $1\,\frac{1}{2}\,\frac{1}{4}$.

Tetrahedral $1\,\frac{1}{2}\,\frac{1}{4}$

$\frac{1}{2}\,1\,0$ Octahedral
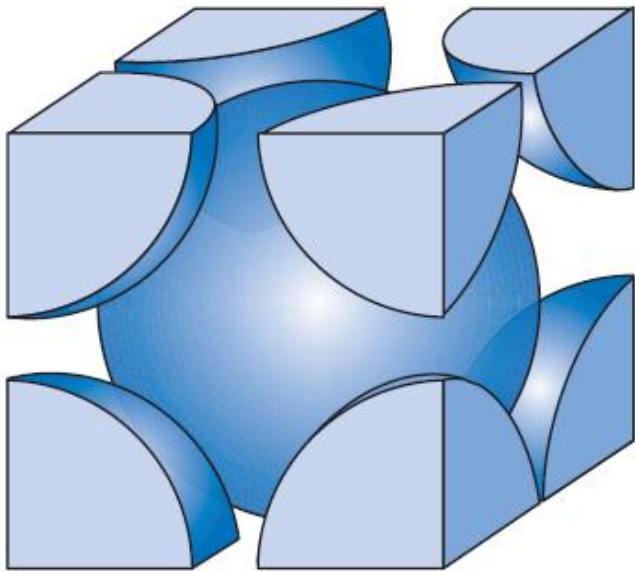
*Locations of tetrahedral and octahedral interstitial sites within **BCC** unit cell*

Interstitial solid solution

BCC unit cell
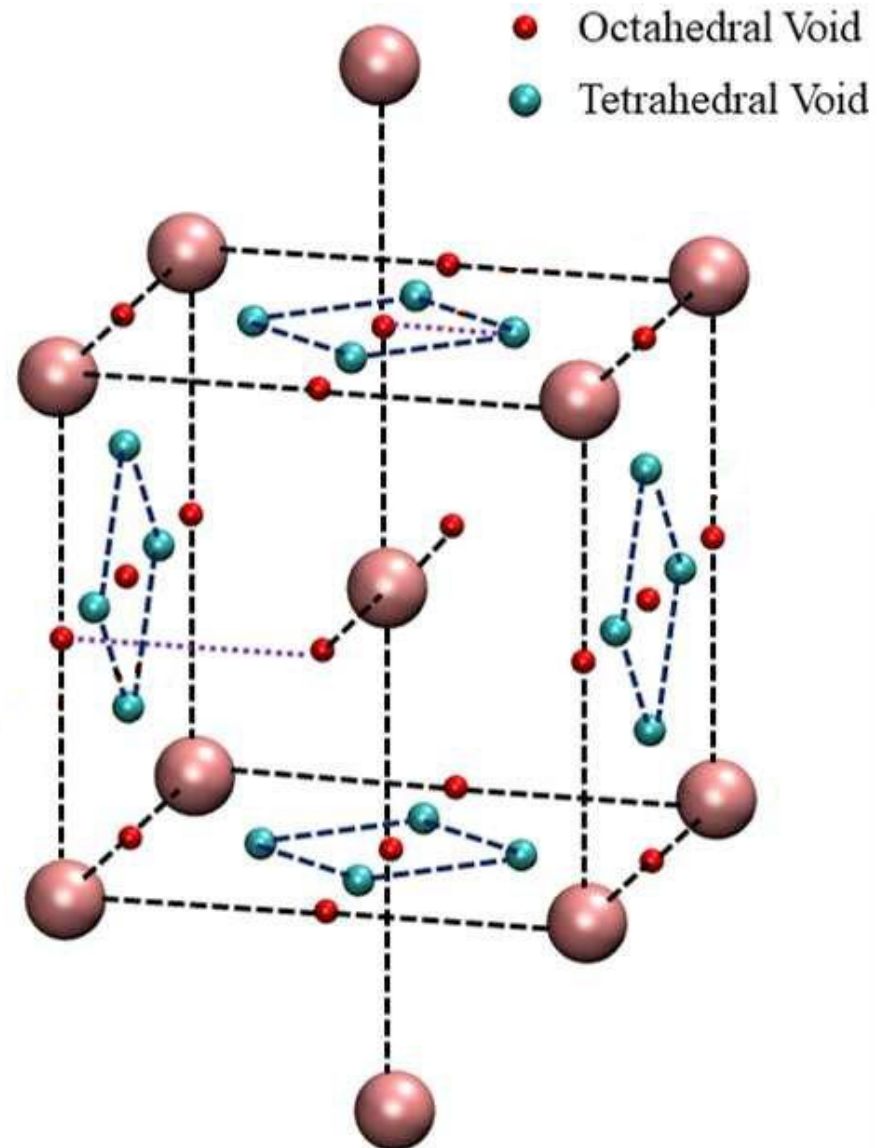
Octahedral Void
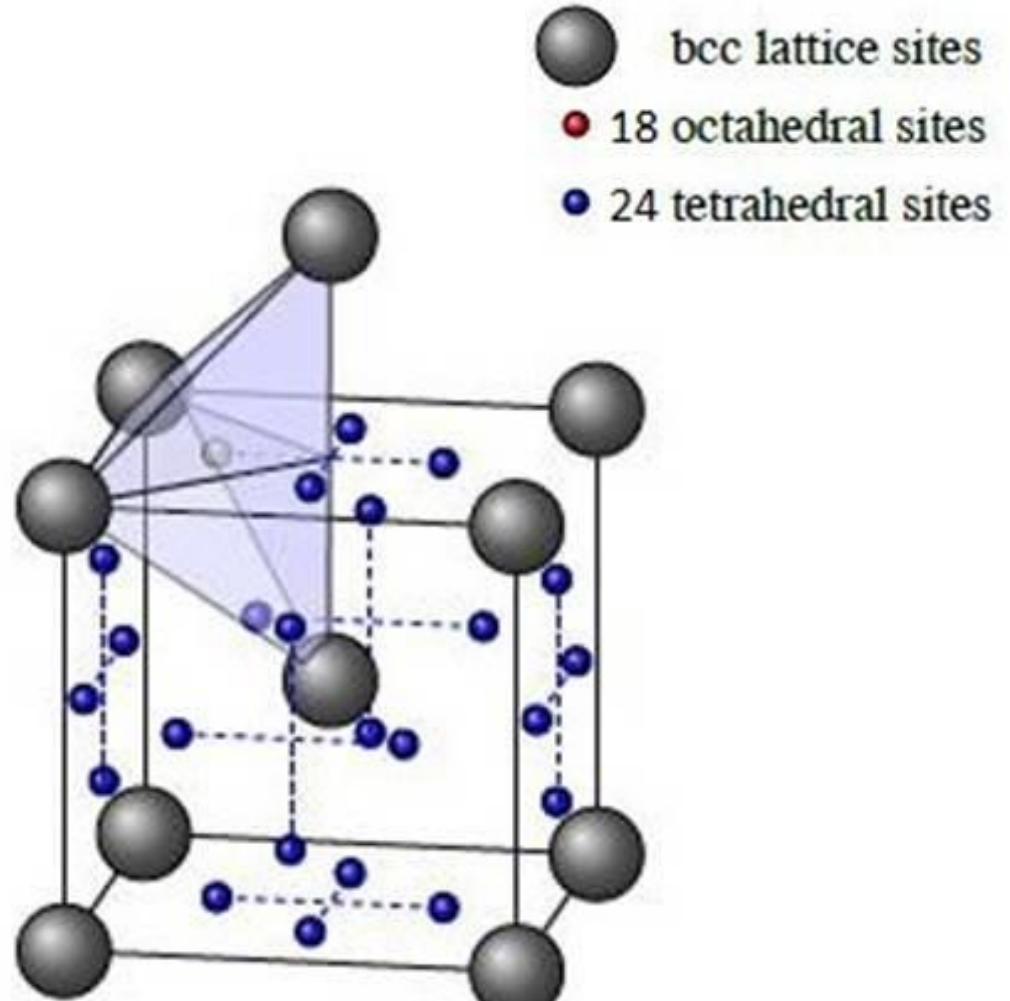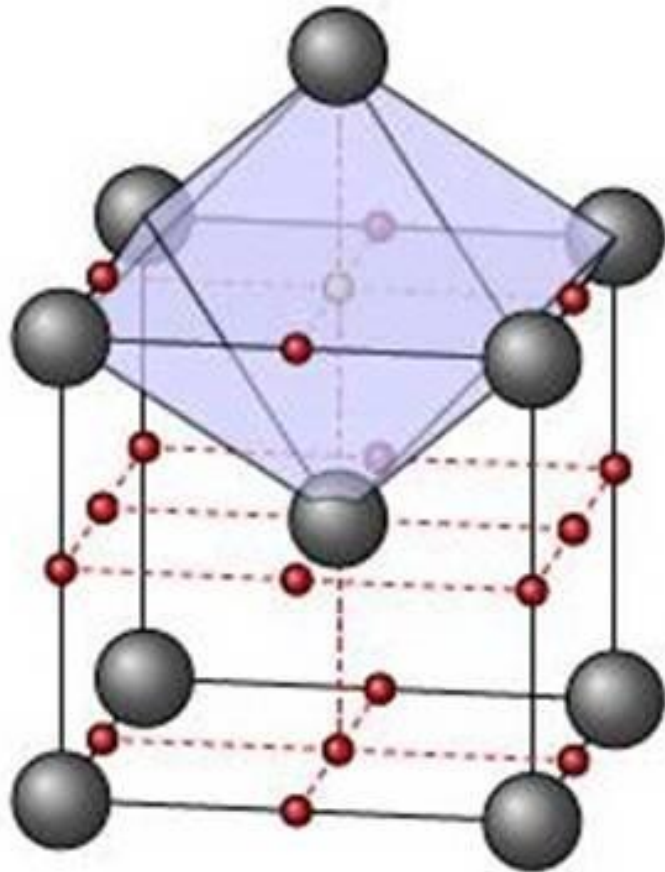Tetrahedral Void

Interstitial solid solution

- bcc lattice sites
- 18 octahedral sites
- 24 tetrahedral sites

4.3. Impurities In Solids

Interstitial solid solution

⦿ **Metallic materials** have relatively **high atomic packing factors**, which means that these **interstitial positions** are **relatively small**.

⦿ Consequently, the **atomic diameter** of an **interstitial impurity must** be **substantially smaller** than that of the **host atoms**.

⦿ Normally, the **maximum allowable concentration** of interstitial impurity atoms is **low** (**less than 10%**).

⦿ **Even very small impurity** atoms are ordinarily **larger** than the **interstitial sites**, and as a consequence, they introduce some lattice strains on the adjacent host atoms.

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Chap 4: Imperfections in Solids

4.4. Specification of Composition

Weight percent

- It is often necessary to express the **composition** (or **concentration**) of an alloy in terms of its **constituent elements**.

- The **two** most **common ways** to specify composition are **weight** (or mass) **percent** and **atom percent**.

- The basis for **weight percent (wt%)** is the weight of a particular element relative to the total alloy weight.

- For an **alloy** that contains **two** hypothetical **atoms** denoted by 1 and 2, the concentration of 1 in wt%, C_1, is defined as

$$C_1 = \frac{m_1}{m_1 + m_2} \times 100$$

where m_1 and m_2 represent the weight (or mass) of elements 1 and 2, respectively.

4.4. Specification of Composition

Weight percent

◉ When an alloy contains **more than two** (say n) **elements**, the equation takes the form:

$$C_1 = \frac{m_1}{m_1 + m_2 + m_3 + \cdots + m_n} \times 100$$

4.4. Specification of Composition

Atom percent

⊙ The basis for atom percent **(at%)** calculations is the **number of moles** of an element **in relation** to the **total moles of the elements in the alloy**.

⊙ The number of moles in some specified mass of a hypothetical element 1, n_{m1}, may be computed as follows:

$$n_{m1} = \frac{m_1'}{A_1}$$

Here, m_1' and A_1 denote the mass (in grams) and atomic weight, respectively, for element 1.

Atom percent

◉ Concentration in terms of **atom percent** of element 1 in an alloy containing element 1 and element 2 atoms, **C'₁** is defined by:

$$C_1' = \frac{n_{m1}}{n_{m1} + n_{m2}} \times 100$$

◉ In like manner, the atom percent of element 2 is determined.

◉ Atom percent computations also can be carried out on the basis of **the number of atoms instead of moles**, because one **mole** of all substances **contains** the **same number** of **atoms**.

4.4. Specification of Composition

Composition Conversions: Conversion of weight percent to atom percent

⊙ Sometimes it is necessary to **convert** from one composition scheme to another—for example, **from weight percent** to **atom percent**.

⊙ We express these conversion equations as follows:

$$C_1' = \frac{C_1 A_2}{C_1 A_2 + C_2 A_1} \times 100$$

$$C_2' = \frac{C_2 A_1}{C_1 A_2 + C_2 A_1} \times 100$$

Composition Conversions: Conversion of atom percent to weight percent

$$C_1 = \frac{C_1' A_1}{C_1' A_1 + C_2' A_2} \times 100$$

$$C_2 = \frac{C_2' A_2}{C_1' A_1 + C_2' A_2} \times 100$$

⊙ Because we are considering only two elements, computations involving the preceding equations are simplified when it is realized that:

$$C_1 + C_2 = 100$$

$$C_1' + C_2' = 100$$

Composition Conversions: **Conversion of weight percent to mass per unit volume**

◉ In addition, it sometimes becomes necessary to convert concentration from **weight percent to mass of one component per unit volume** of material (i.e., from units of **wt%** to **kg/m³**).

◉ Concentrations in terms of this basis are denoted using a double prime (i.e., **C''₁ and C''₂**), and the relevant equations are as follows:

$$C_1'' = \left(\frac{C_1}{\dfrac{C_1}{\rho_1} + \dfrac{C_2}{\rho_2}} \right) \times 10^3$$

$$C_2'' = \left(\frac{C_2}{\dfrac{C_1}{\rho_1} + \dfrac{C_2}{\rho_2}} \right) \times 10^3$$

4.4. Specification of Composition

Computation of density and atomic weight

◉ For density ρ in units of **g/cm^3**, these expressions yield **C"$_1$ and C"$_2$** in **kg/m^3**.

◉ Furthermore, on occasion we desire to determine the **density** and **atomic weight** of a binary alloy, given the composition in terms of either **weight percent** or **atom percent**.

◉ If we represent alloy density and atomic weight by $\boldsymbol{\rho_{ave}}$ and $\mathbf{A_{ave}}$, respectively, then:

$$\rho_{ave} = \frac{100}{\dfrac{C_1}{\rho_1} + \dfrac{C_2}{\rho_2}}$$

$$\rho_{ave} = \frac{C_1' A_1 + C_2' A_2}{\dfrac{C_1' A_1}{\rho_1} + \dfrac{C_2' A_2}{\rho_2}}$$

$$A_{ave} = \frac{100}{\dfrac{C_1}{A_1} + \dfrac{C_2}{A_2}}$$

$$A_{ave} = \frac{C_1' A_1 + C_2' A_2}{100}$$

4.4. Specification of Composition

- It should be noted that the Equations are **not always exact**.

- In their derivations, it is **assumed** that **total alloy volume** is **exactly equal** to the **sum** of the **volumes** of the **individual elements**.

- This normally is **not the case** for most alloys; however, it is a reasonably **valid assumption** and does **not lead to significant errors** for dilute solutions and over composition ranges where solid solutions exist.