Point Defects

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Why we should study the Defects?

- Structural discontinuity and localized disorder regions are always present in real solids.

- With defects or imperfections, heterogeneity can exits on microscopic and macroscopic scales.

Many properties can be altered by the defects/impurities

For example

- Ni-, Co-, Ti- based superalloys have better mechanical properties compare to the pure metals.

- Doped semiconductors show much low resistivity compare to pure semiconductors.

- Absorption or emission of different wavelengths of light by any material can be altered with defects.

Classifications of Defects?

Based on Dimensionality

0D (Point Defects)

- Vacancy
- Impurity
- Substitution
- Frenkel defects
- Schottky defects

1D (Line Defects)

- Dislocation
- Disclination

2D (Surface/Interface)

- Surface
- Grain boundary
- Interphase boundary
- Twin boundary
- Stacking faults

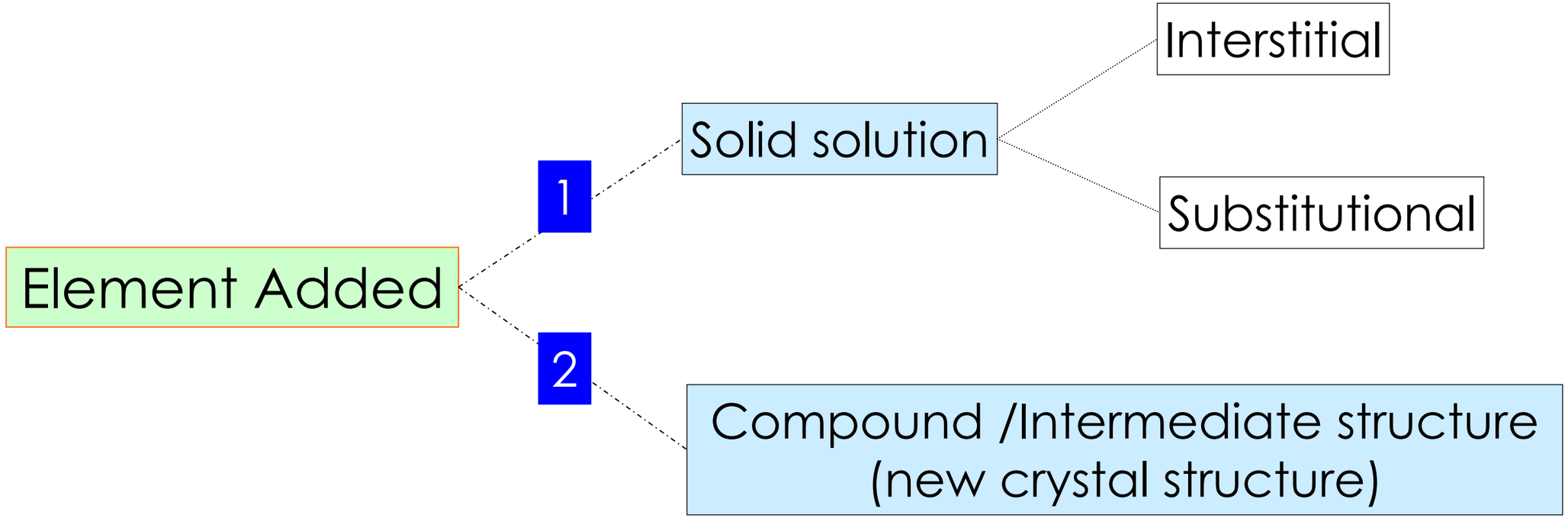
3D (Volume Defects)

- Twin
- Precipitates
- Faulted regions
- Voids/cracks

Some basic terms

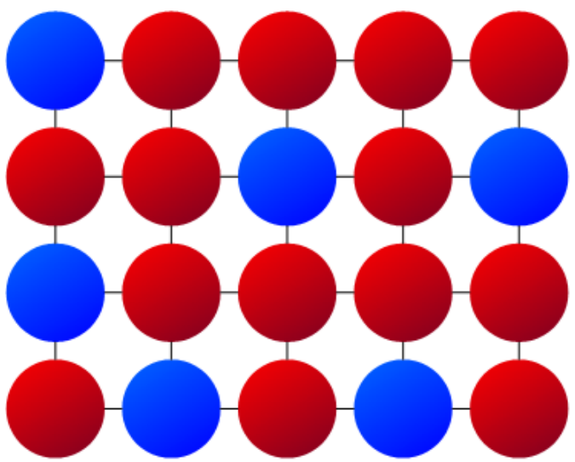
Alloying

- In a pure material when other elements are added intentionally they are called alloying elements.
- When added small quantity it is often called doping
- There is no difference between an '*impurity*' and '*alloying*

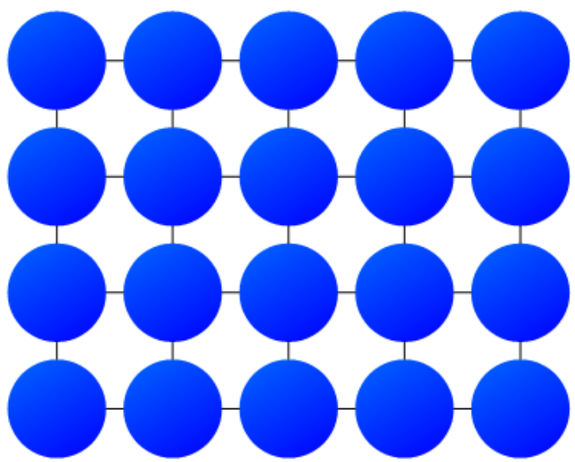


Some basic terms

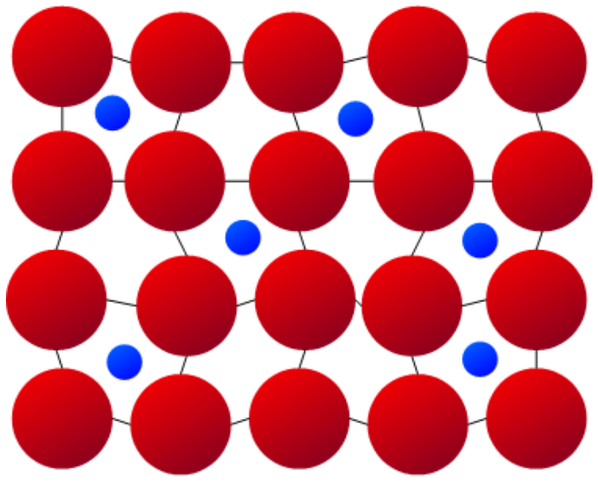
Substitution and interstitial solid solutions



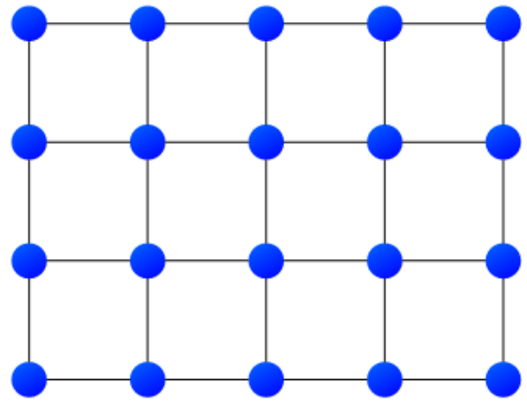
substitution of individual host atoms A by alloying atoms B



alloying element B



deposition of individual alloying atoms B in the lattice of the host component A



alloying element B

Some basic terms

Substitution and interstitial solid solutions

Solid solutions

The mixing is at the atomic scale and is analogous to a liquid solution.

HUME ROTHERY RULES

Empirical rules for the formation of substitutional solid solution

1. The solute and solvent atoms do not differ by more than 15% in diameter.
2. The electronegativity difference between the elements is small.
3. The valency of the elements is same.
4. The crystal structure of the elements is same.

Additional rule

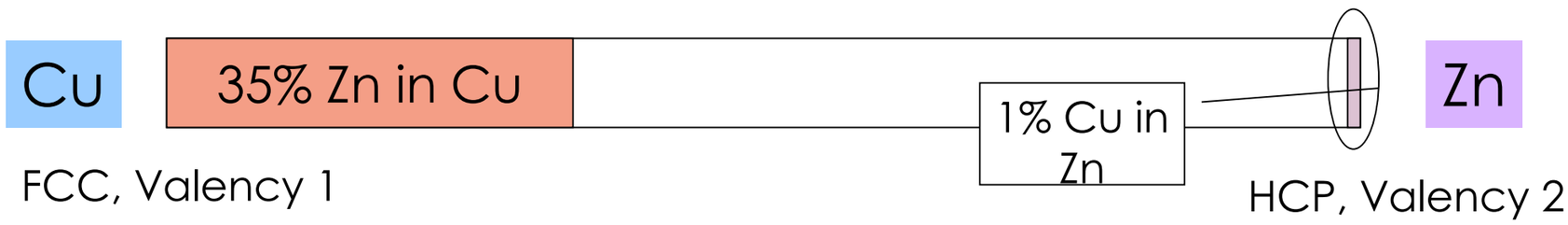
- Element with higher valency is dissolved more in an element of lower valency rather than vice-versa.

Some basic terms

Example Hume-Rothery rule

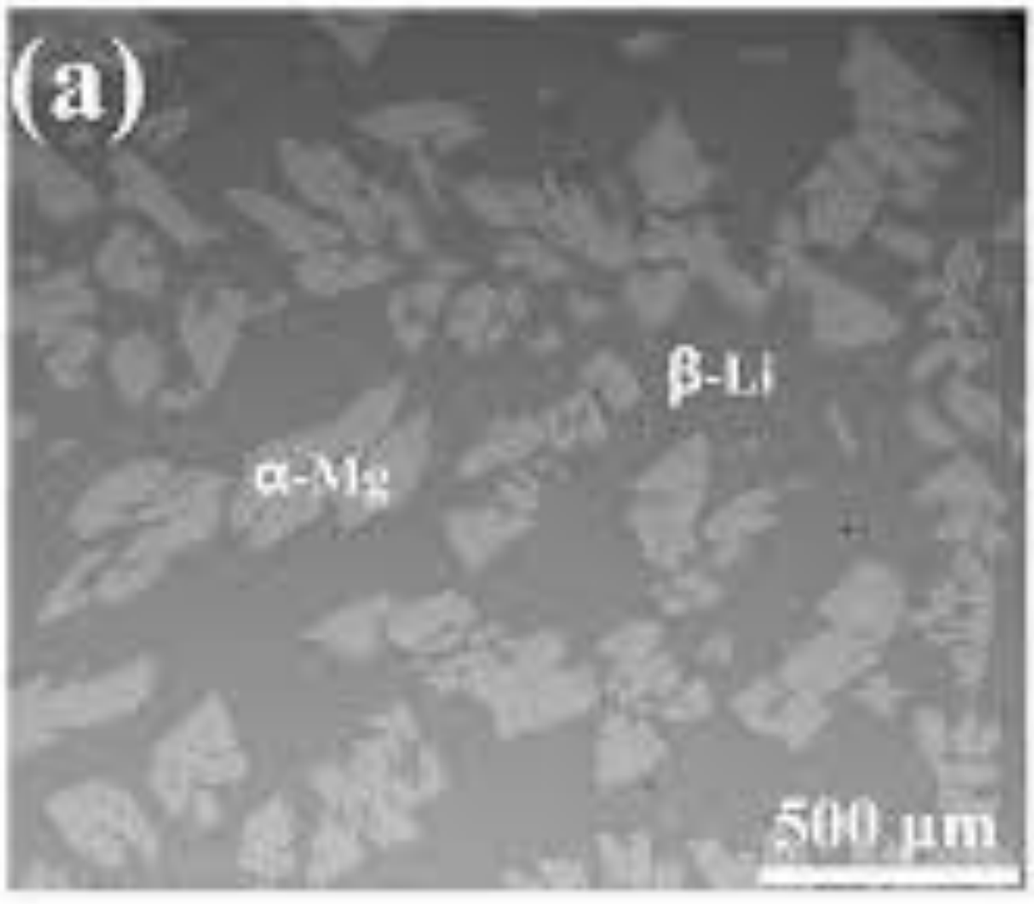
System		Crystal structure	Radius of atoms (Å)	Valency	Electronegativity
Ag-Au	Ag	FCC	1.44	1	1.9
	Au	FCC	1.44	1	2.4
Cu-Ni	Cu	FCC	1.28	1	1.9
	Ni	FCC	1.25	2	1.8
Ge-Si	Ge	DC	1.22	4	1.8
	Si	DC	1.18	4	1.8

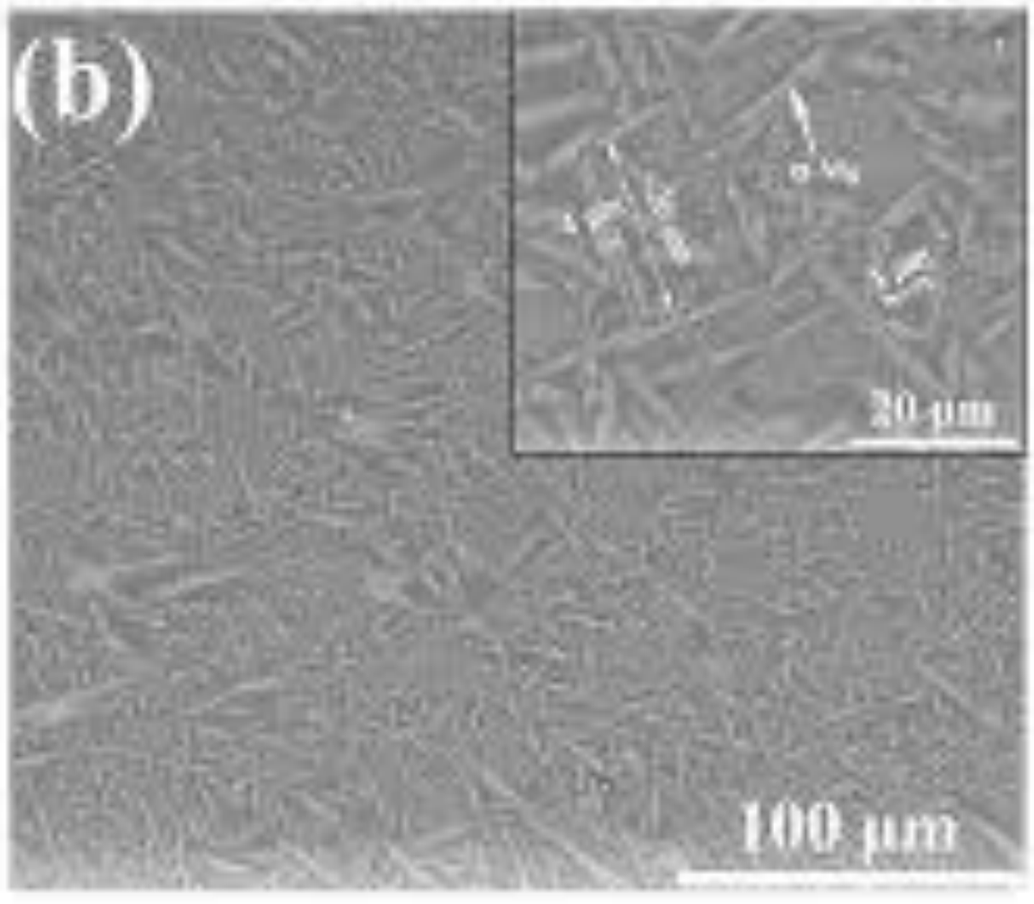
Example of a pair of elements not forming solid solution in all proportions



Some basic terms

Examples of Alloy and Solid solutions





Solid solutions is atomic level mixing

Point Defects (zero dimensional)

Non-Ionic Crystals ⟷ Ionic Crystals

1.Vacancy

2.Impurity (alloying element/dopants)

- Interstitial
- Substitutional

1.Frenkel Defects

2.Schottky Defects

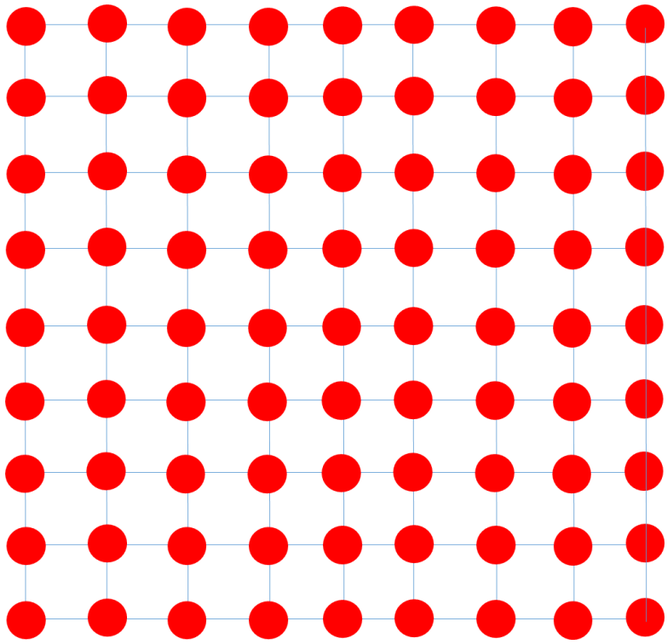
- Charge neutrality condition should meet. Means number of positive and negative from the ions should be equal (Defects in ceramics do not occur alone)

❑Size or regions of point defect ~ 1-2 atomic diameter and distorted regions can be extends to large distances

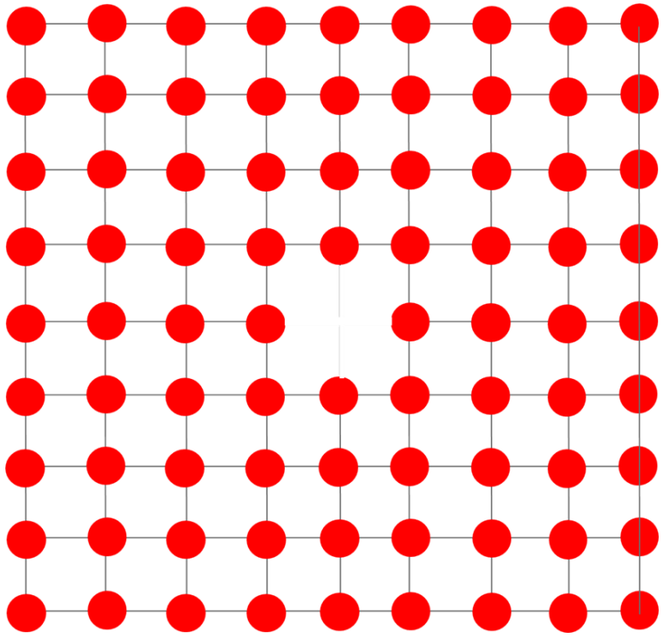
❑Point defects can be created by removal or addition or displacement of an atomic species (atoms, ions) from lattice site

Point Defects (zero dimensional):Non-Ionic Solids

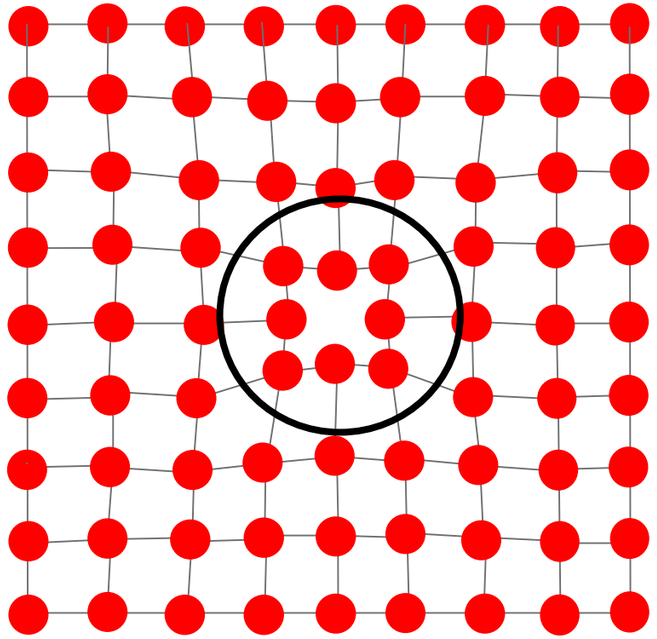
Vacancy



Perfect crystal



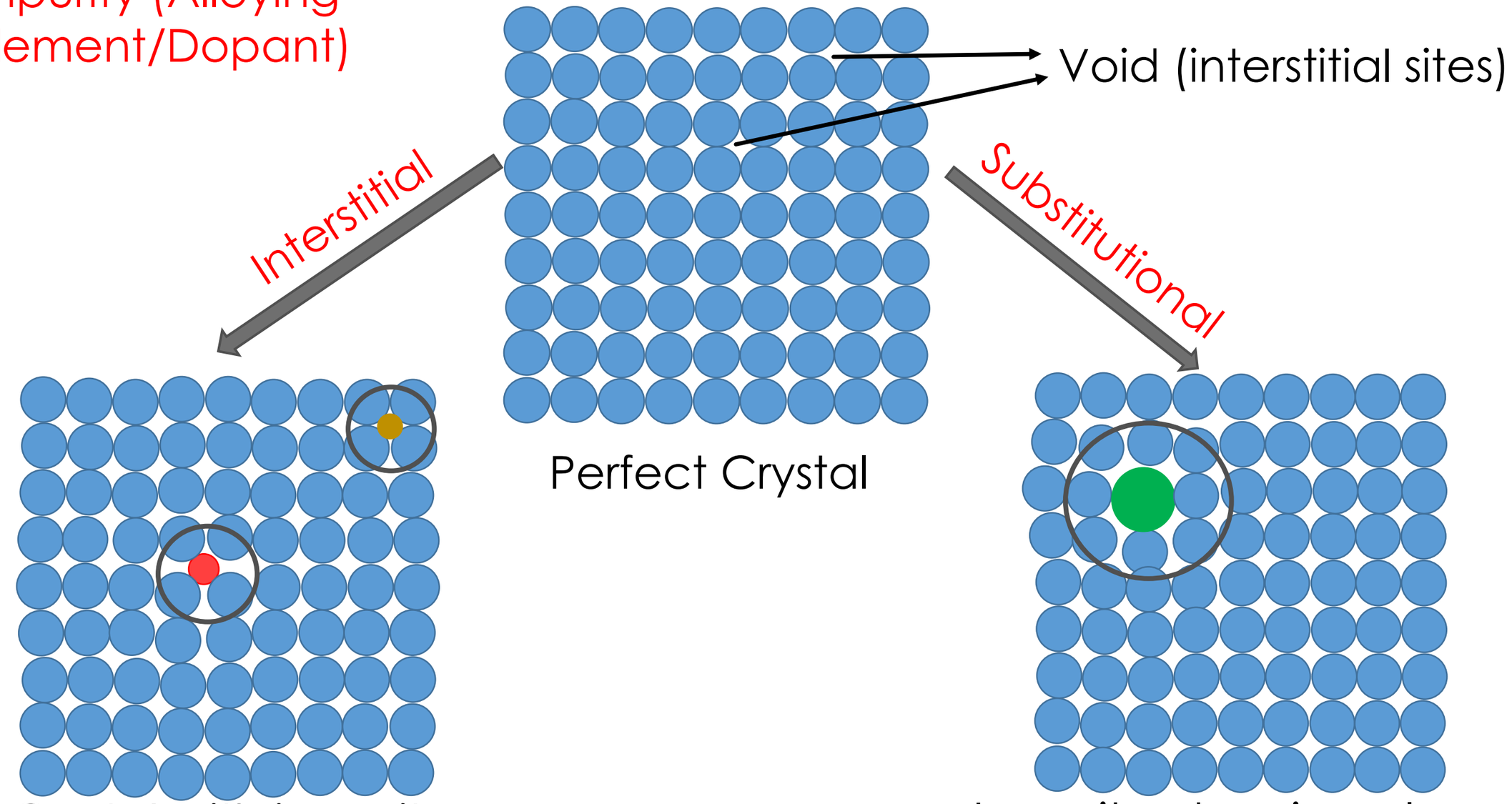
Atom is missing from lattice site
(creation of vacancy)



Lattice strain around the vacancy

Point Defects (zero dimensional)):Non-Ionic Solids

Impurity (Alloying element/Dopant)



Perfect Crystal

Crystal with impurity atom sitting in the voids

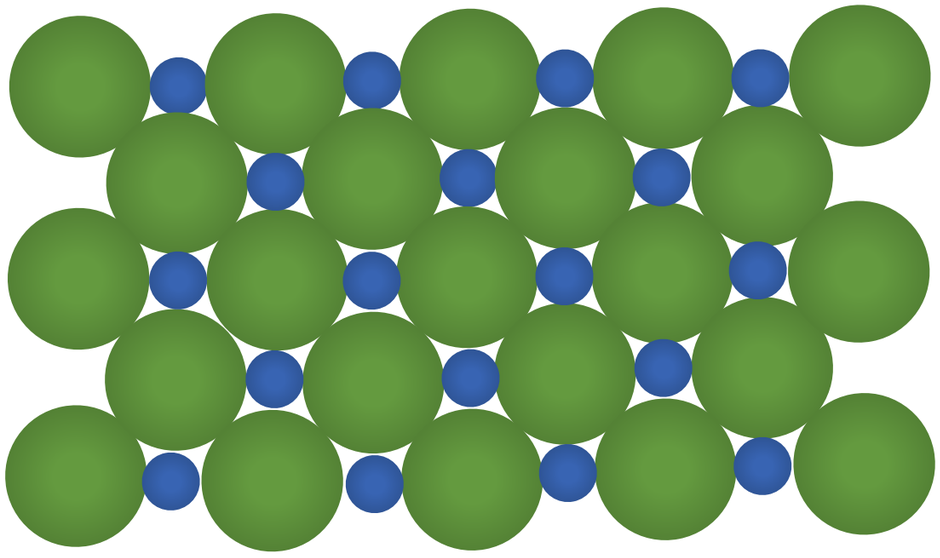
Impurity atom is replaced with parent atom of crystal

Point Defects (zero dimensional): Ionic Solids

Perfect Crystal

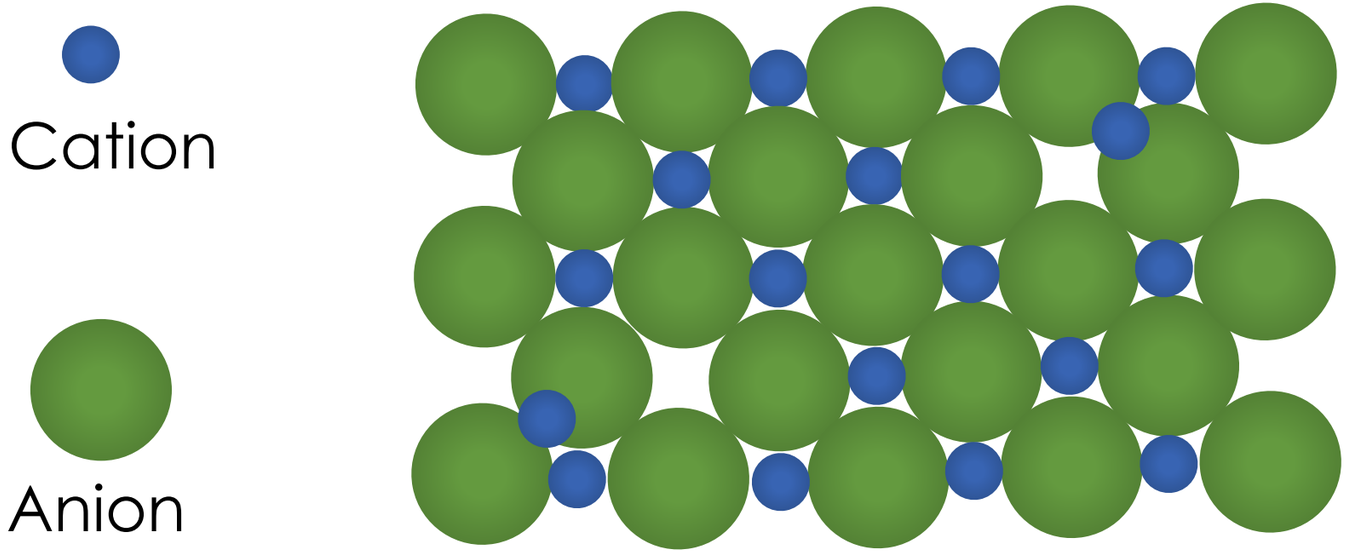
Cation

Anion



Point Defects (zero dimensional): Ionic Solids

Frenkel Defect



- Cation being smaller displaced to interstitial sites
- Charge neutrality maintained
- No change in density
- Examples: NaCl, AgBr, KCl, CaF_2

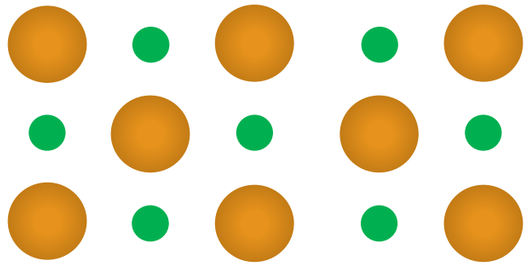
Point Defects (zero dimensional): Ionic Solids

Impurities (Ionic Solids)

Must satisfy charge neutrality condition

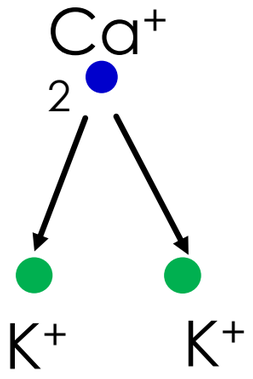
Example: KCl K^+ Cl^-

❑Substitutional cation impurity

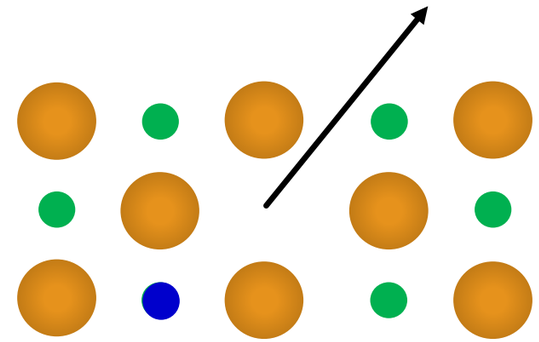


Initial geometry

Replaced

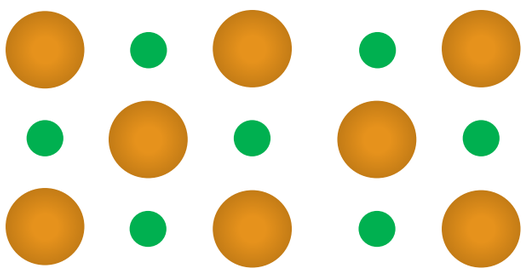


Cation impurity



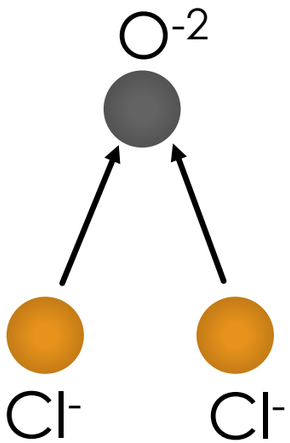
Final geometry

❑Substitutional anion impurity

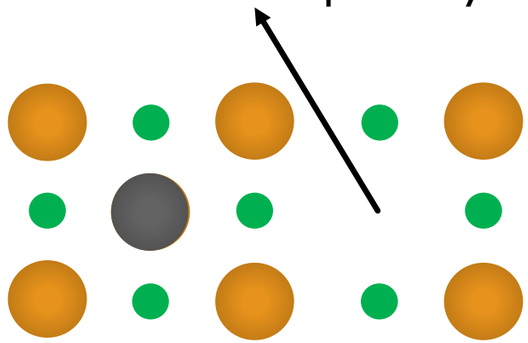


Initial geometry

Replaced



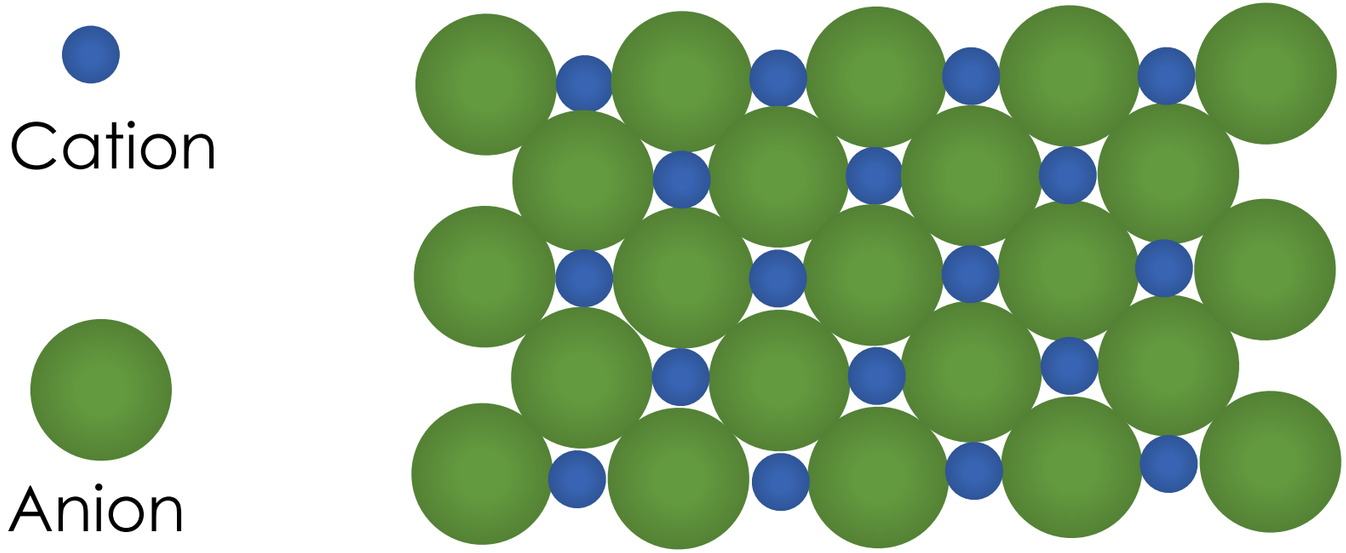
Anion impurity



Final geometry

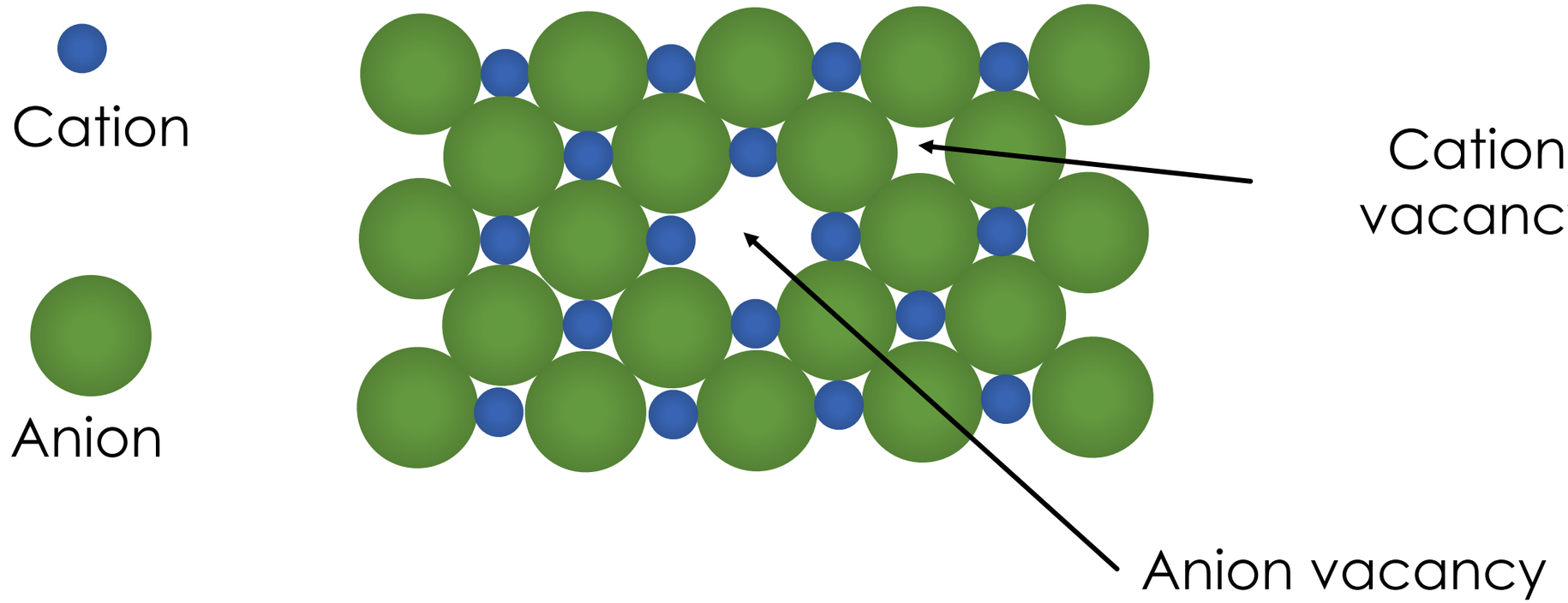
Point Defects (zero dimensional): Ionic Solids

Perfect Crystal



Point Defects (zero dimensional): Ionic Solids

Schottky Defect



- A Pair of anion and cation missing
- Charge neutrality maintained
- Change in density
- Examples: NaCl, AgBr, KCl, CaF_2

Concentration of point defects

Change in free energy of crystal when we add n point defects in one mole of crystal

$$\Delta G = \Delta H - T\Delta S = n\Delta H_f - kT[NlnN - (N-n)\ln(N-n) - nlnn]$$

Where N is the Avogadro number

At equilibrium,

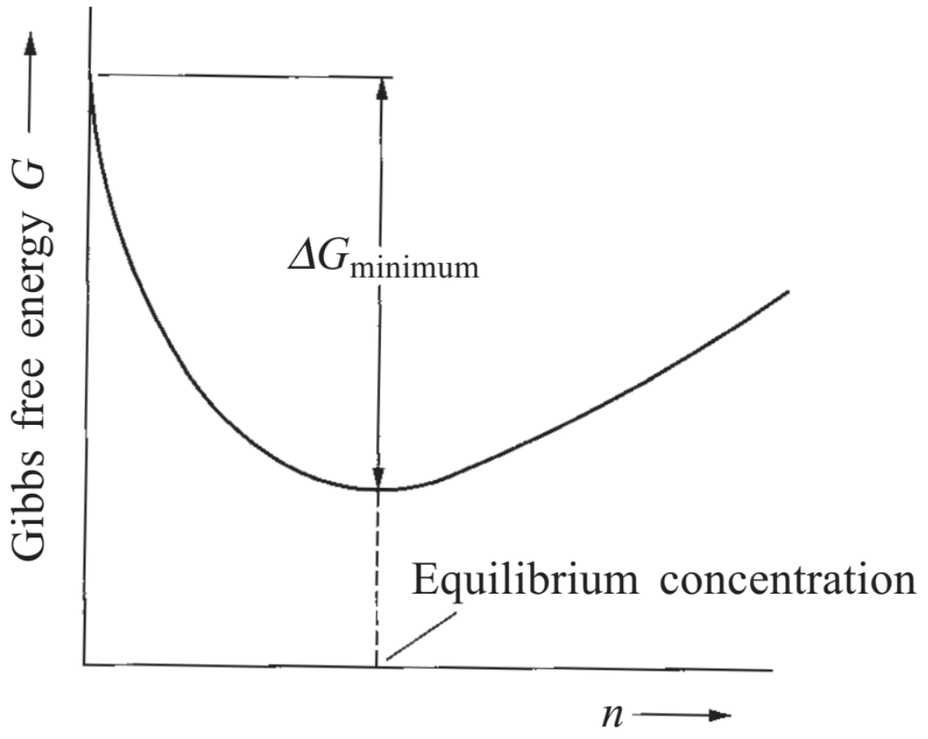
$$\frac{d\Delta G}{dn} = 0$$

$$\boxed{\frac{n}{N} = \exp.(-\frac{H_f}{RT})}$$

Where R is gas constant

OR

$$\boxed{\frac{n}{N} = \exp.(-\frac{Q_d}{kT})}$$



Where N, Q and k is the Avogadro number, activation energy and Boltzmann constant respectively.

Concentration of point defects in ionic solids

$$\frac{n}{N} = \exp.(-\frac{H_f}{2RT})$$

Where R is gas constant

OR

$$\frac{n}{N} = \exp.(-\frac{Q_d}{2kT})$$

Where N, Q and k is the Avogadro number, activation energy and Boltzmann constant respectively

The factor 2 appears because the energy of formation HF or Qd refers to the formation of the defect pair.

Summary

1. Hume-Rothery condition is for the formation of solid solutions.
2. Defects can alter the properties of the materials.
3. Frenkel and Schottky defects takes place only in ionic solids.
4. Charge neutrality must be maintained in ionic solids.
5. Solid solutions is the atomic level mixing of atoms.

Assignment

1. FCC lead has a lattice parameter of 0.4949 nm and contains one vacancy per 500 Pb atoms. Calculate (a) the density; and (b) the number of vacancies per gram of Pb.
2. Determination of the number of vacancies per cubic meter in gold at 900 °C. Given that the formation energy of the defect is 0.98 eV/atom, atomic weight is 197 g/mol and density of 19.32 g/cm^3.
3. Calculate the activation energy for vacancy formation in aluminum, given that the equilibrium number of vacancies at 500 C is 7.57 x 10^{23} m^{-3}. The atomic weight and density for aluminum are, respectively, 26.98 g/mol and 2.62 g/cm^3.
4. Average energy required to create Frenkel defect in an ionic crystal is 1.4 eV. Calculate the ratio of Frenkel defects at 20°C and 300°C in 1 gram of crystal.