Lecture 11
M 19.08.2025

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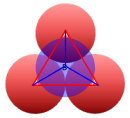
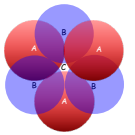
Voids in Close-Packed Crystals

	TETRAHEDRAL VOID	OCTAHEDRAL VOID
		 Octahedron seen along its Fourfold axis: Triangular antiprism
No. of atoms defining the void	4	6
No. of voids per atom	2	1 Experiment 5
Edge length	$2R$	$2R$
Size of the void	$r = 0.225\ R$?	$r = 0.414\ R$ HW

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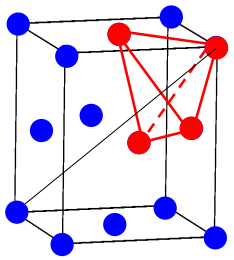
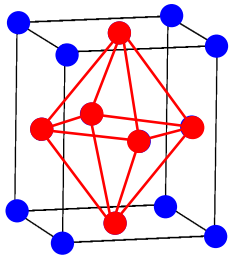
Location of Voids in CCP Unit cell



Eight voids per Unit cell with centroids on the body diagonals



Four voids per Unit cell with centroids on the body centre and edge cenre

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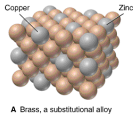
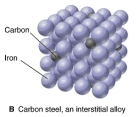
Solid Solution

A single crystalline phase consisting of two or more elements is called a solid solution.



A Brass, a substitutional alloy

Substitutional Solid solution of Cu and Zn (FCC)



B Carbon steel, an interstitial alloy

Interstitial solid solution of C in Fe (BCC)

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Hume-Rothery Rules for Extensive Solid Solution (Unlimited solubility)

~~Interstitial solid solution~~ Substitutional solid solution

1. **Structure factor**

   Crystal structure of the two elements should be the same

2. **Size factor:**

   Size of the two elements should not differ by more than 15%

3. **Electronegativity factor:**

   Electronegativity difference between the elements should be small

4. **Valency factor:**

   Valency of the two elements should be the same

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TABLE 5.2

System		Crystal structure	Radius of atoms, Å	Valency	Electro-negativity
Ag-Cu	Ag	FCC	1.44	1	1.9
	Au	FCC	1.44	1	1.9
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

All three systems exhibit complete solid solubility.

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Your relationship to Hume-Rothery

Prof. William Hume-Rothery (Oxford) — Great Great Grand father

↓

Prof. J.W. Christian (Oxford) — Great Grand father

↓

Prof. T.R. Anantharaman (BHU) — Grand father

↓

Rajesh Prasad — father

↓

You

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BRASS

Cu + Zn

FCC HCP

Unfavourable structure factor

Limited Solubility:

Max solubility of Cu in Zn: 1 wt% Cu

Max Solubility of Zn in Cu: 35 wt% Zn

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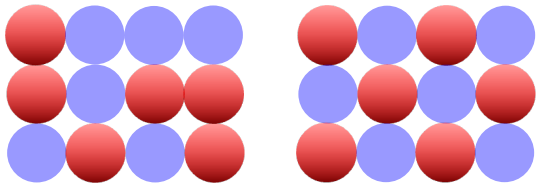
Ordered and Random
Substitutional solid solution



Random Solid Solution

Ordered Solid Solution

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IONIC SOLIDS

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IONIC SOLIDS

Cation radius: R^+
Anion radius: R^-

Usually $R^- > R^+$

1. Cation and anion attract each other.

2. Cation and anion spheres touch each other

3. Ionic bonds are non-directional

1, 2, 3 => Close packing of unequal spheres

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IONIC SOLIDS

Local packing geometry

1. Anions and cations considered as hard spheres always touch each other.
2. Anions generally will not touch, but may be close enough to be in contact with each other in a limiting situation.
3. As many anions as possible surround a central cation for the maximum reduction in electrostatic energy.

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Effect of radius ratio

$\frac{R_c}{R_a} < 0.155$ unstable

Anions not touching the central cation,

Anions touching each other

$\frac{R_c}{R_a} = 0.155$ Critically stable

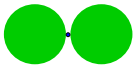
Anions touching the central cation

Anions touching

$\frac{R_c}{R_a} > 0.155$ stable

Anions touching central cation

Anions not touching each other



$\frac{R_c}{R_a} < 0.155 \Rightarrow Ligancy = 2$

$\frac{R_c}{R_a} \geq 0.155 \Rightarrow Ligancy = 3$

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$\frac{R_c}{R_a} \geq 0.155 \Rightarrow Ligancy = 3$

However, when $\frac{R_c}{R_a} \geq 0.225$ tetrahedral coordination with ligancy 4 becomes stable

Recall tetrahedral void in close-packed structure.

Thus

$$0.155 < \frac{R_c}{R_a} \leq 0.225 \Rightarrow Ligancy = 3$$

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Table 5.3

Ligancy as a Function of Radius Ration

Ligancy	Range of radius ratio	Configuration
2	0.0 — 0.155	Linear
3	0.155 — 0.225	Triangular
4	0.225 — 0.414	Tetrahedral
6	0.414 — 0.732	Octahedral
8	0.732 — 1.0	Cubic
12	1.0	FCC or HCP

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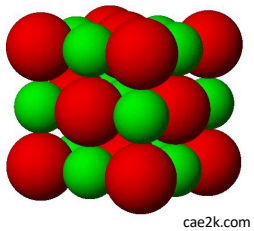
Example 1:
NaCl



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$\frac{R_{Na^+}}{R_{Cl^-}} = 0.54$

$0.414 < 0.54 < 0.732$

$\Rightarrow Ligancy\ 6$

Octahedral Coordination

NaCl structure =FCC lattice + 2 atom motif: Cl^- 0 0 0
Na $\frac{1}{2}$ 0 0

Examples:
NaCl, KCl, TiC, MgO, PbS

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