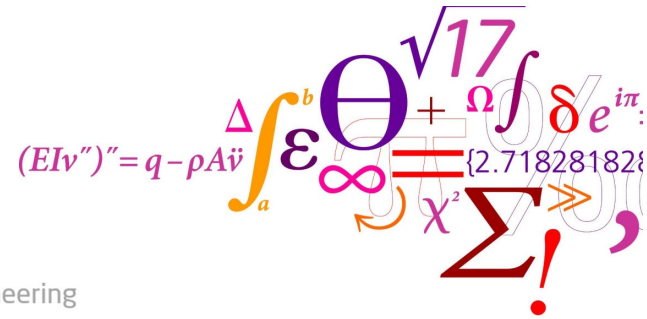
Lattice defects

Is order everything?

41680 Introduction to advanced materials



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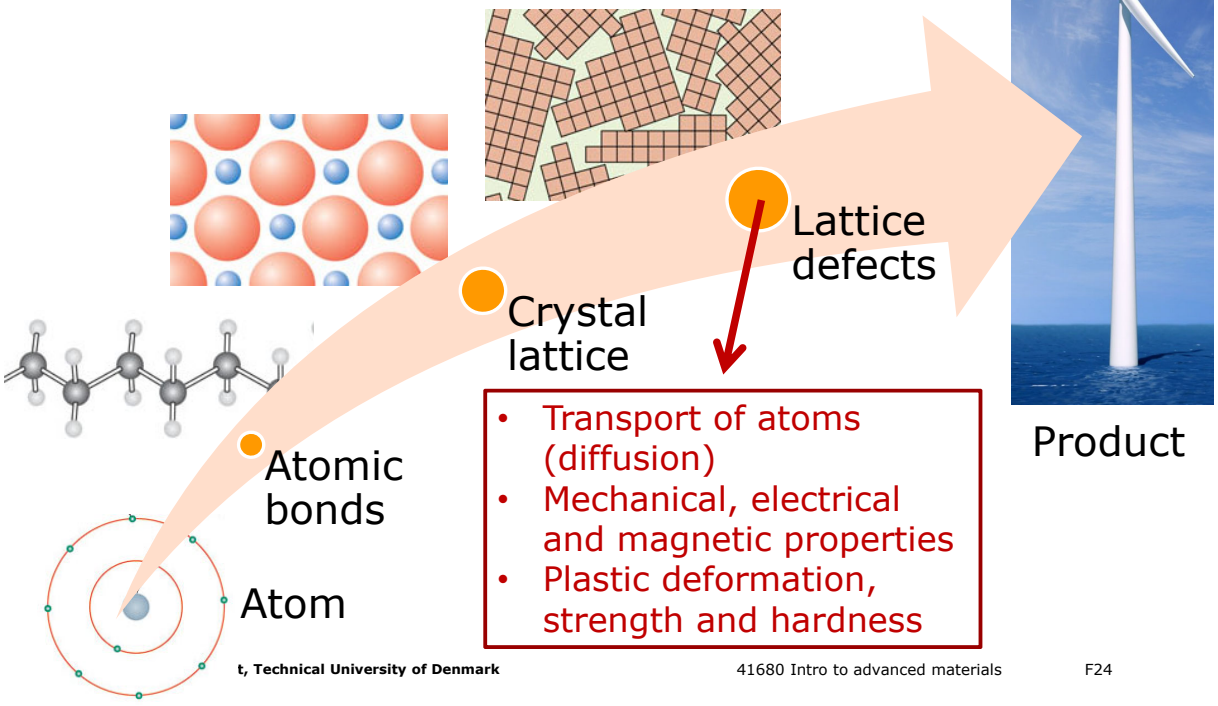
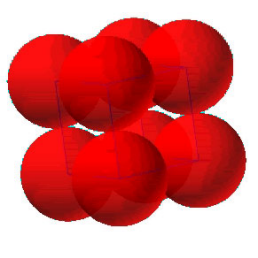
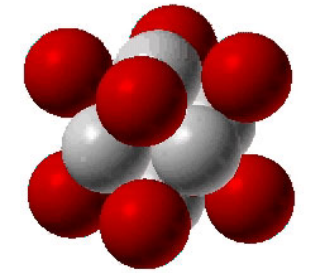
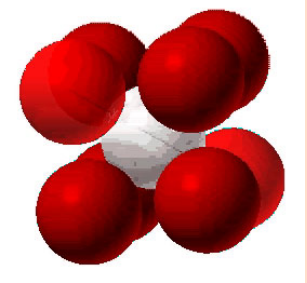
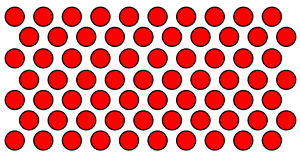
Advanced materials
Atoms - Microstructure - Properties



Cubic lattices

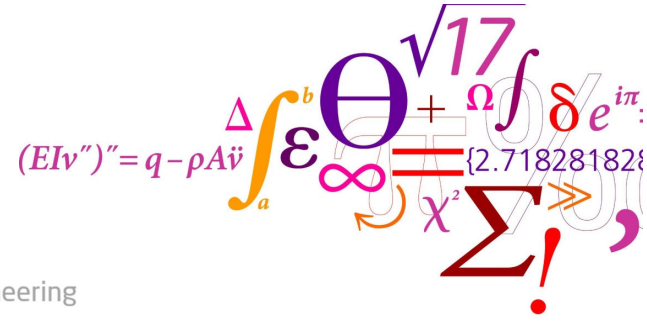
Simple cubic (sc)	Face-centered cubic (fcc)	Body-centered cubic (bcc)
		
Elements	Al, Cu, Ni, Ag, Au, Pt, γ-Fe	α-Fe, V, Nb, Ta, Cr, Mo, W, K
Atomic packing factor	74 %	68 %
Packing of planes	Close-packed planes	Less dense planes



Lattice defects

41680 Introduction to advanced materials

„Crystals are like people, it is the defects in them, which make them interesting!"
(Colin Humphreys)



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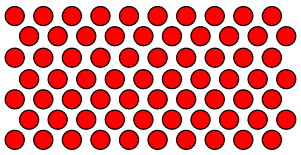


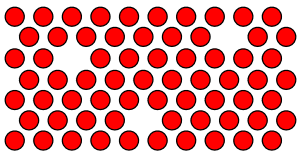
Lattice defects

0-dimensional: point defects
vacancies, interstitials, substitutional atoms

1-dimensional: line defects
dislocations

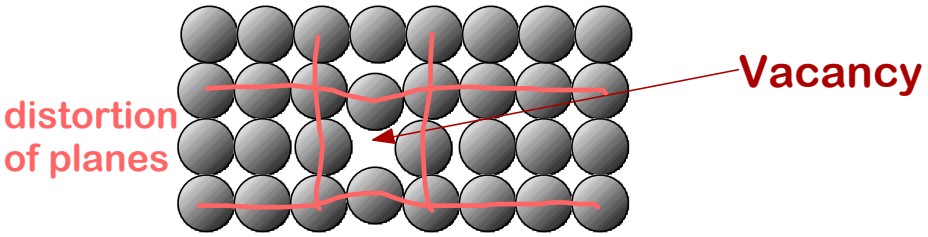
2-dimensional: area (planar) defects
interfaces (stacking faults,
grain-, phase-, twin-boundaries, surfaces)

3-dimensional: volume (bulk) defects
voids, pores, precipitates, inclusions, cracks



Point defects
Vacancies

- Vacant lattice site in a lattice

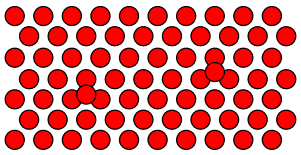


- Vacancies exist in thermal equilibrium
- Equilibrium density of vacancies

$$c_V = \frac{N_V}{N} = e^{-\frac{Q_V}{kT}}$$

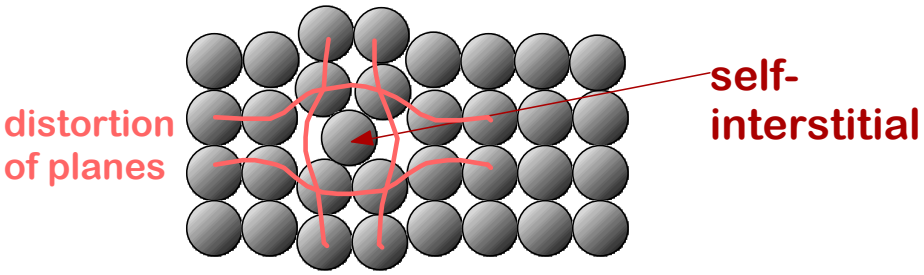
N_V number of vacancies
N number of lattice sites
Q_V vacancy formation energy (G_V)
k =1.38·10^{-23} J/K Boltzmann constant

- Concentration at melting point 10^{-4}



Point defects
Self-interstitial atoms (SIA)

- Atoms sitting on an interstitial site (between lattice sites)



- High formation energy:
  No self-interstitial atoms in thermal equilibrium in metals
- High mobility

Lattice defects

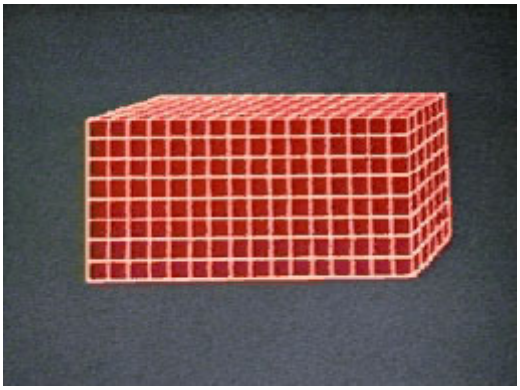
0-dimensional: point defects
vacancies, interstitials, substitutional atoms

1-dimensional: line defects
dislocations

2-dimensional: area (planar) defects
interfaces (stacking faults,
grain-, phase-, twin-boundaries, surfaces)

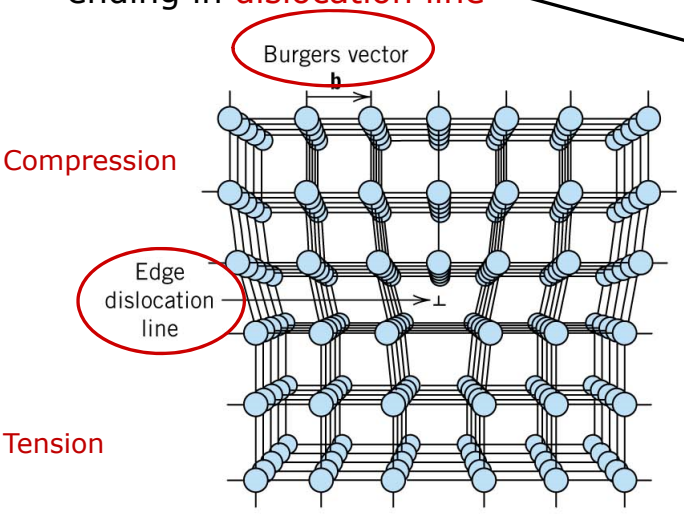
3-dimensional: volume (bulk) defects
voids, pores, precipitates, inclusions, cracks

Motion of (edge) dislocation



Line defects
Dislocations

Extra lattice plane inserted in crystal,
not extending through all of the crystal (half-plane),
ending in dislocation line



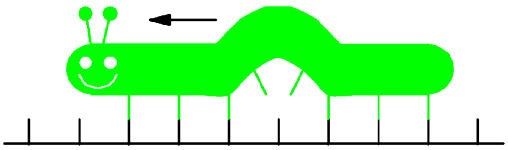
Lattice disturbed along line
→ one-dimensional defect

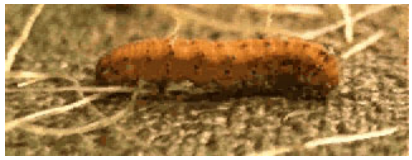
Edge dislocation

Burgers vector
(displacement vector)
- is a lattice vector
- defines slip direction

Line defects
Dislocations as carrier of plastic deformation

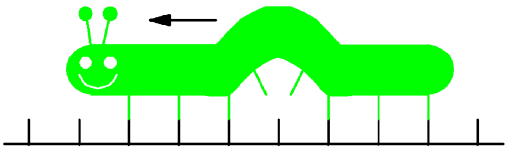
- Caterpillar technique

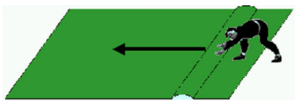


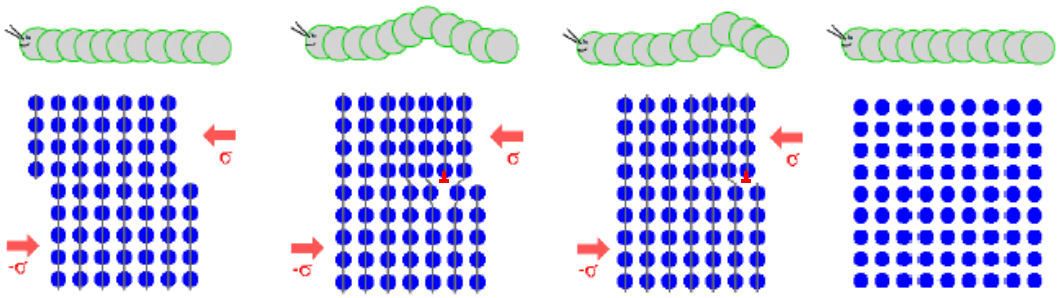


Line defects
Dislocations as carrier of plastic deformation

- Caterpillar technique
- same trick as moving a carpet







4 3 2 1

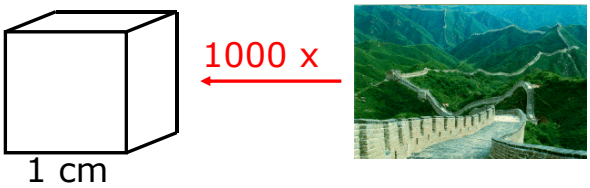
plastic deformation proceeds – atomic step by atomic step
– by movement of dislocations

Line defects
Dislocation density

- Definition (dislocation line length per volume)

$$\rho = \frac{L}{V}$$

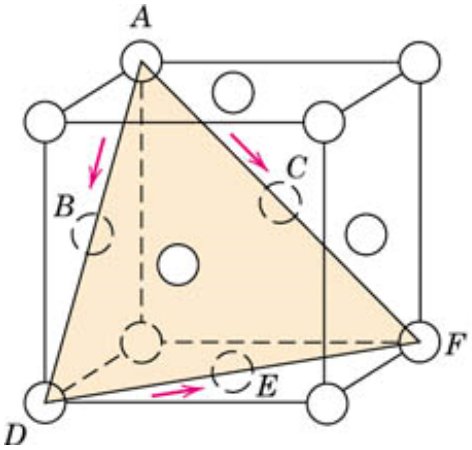
- SI unit $m/m^3 = m^{-2}$
- Whiskers containing a single (screw) dislocation
- Si wavers 10^4 m^{-2}
- Undeformed metals 10^{10} m^{-2}
- Highly deformed metals 10^{16} m/m^3
  - Illustration: 10 million km in a cm^3



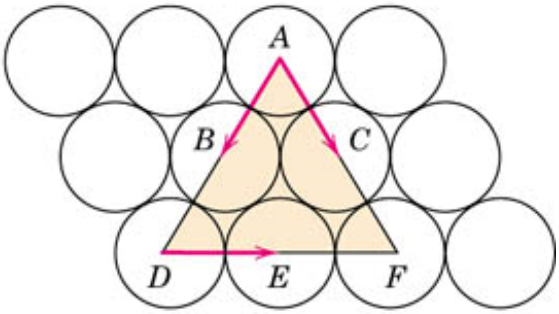
Dislocations and crystalline lattice

Slip systems in metals

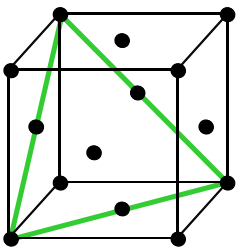
- plastic deformation = dislocation motion = slip (or glide)
- slip system: slip plane {hkl} + slip direction <uvw>
  closest packed plane + closest packed direction
  planes with largest distance + Burgers vector



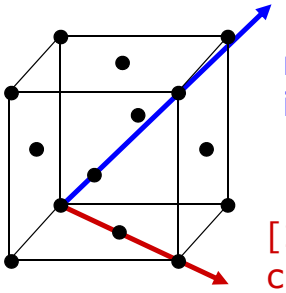
Example: fcc lattice



Close-packed planes (hkl) and directions [uvw]



fcc

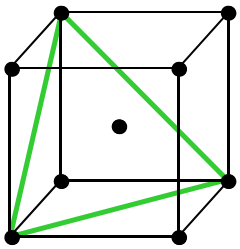


[111] = not close-packed in fcc

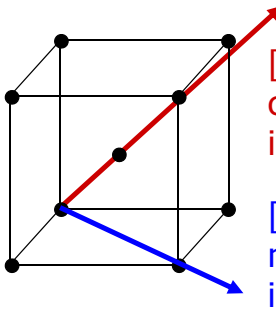
[110] = close-packed in fcc

(111) plane: close-packed in fcc,

but not in bcc



bcc



[111] = close-packed in bcc

[110] = not close-packed in bcc

Slip systems in metals

- plastic deformation = dislocation motion = slip (or glide)
- slip system: slip plane {hkl} + slip direction <uvw>
  closest packed plane + closest packed direction
  planes with largest distance + Burgers vector

Lattice	Examples	Close(st) packed planes (hkl)	Close(st) packed directions [uvw]	Slip systems
fcc	Al, Cu, Ag, Au, Ni, γ-Fe, …	{111} = close-packed	<110> face diagonals	4 x 3 = 12
bcc	Cr, W, α-Fe, …	{110} = not close-packed	<111> volume diagonals	6 x 2 = 12

Lattice defects

0-dimensional: point defects
vacancies, interstitials, substitutional atoms

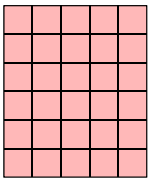
1-dimensional: line defects
dislocations

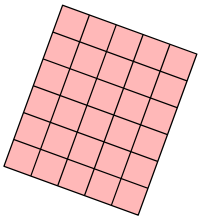
2-dimensional: area (planar) defects
interfaces (stacking faults,
grain-, phase-, twin-boundaries, surfaces)

3-dimensional: volume (bulk) defects
voids, pores, precipitates, inclusions, cracks

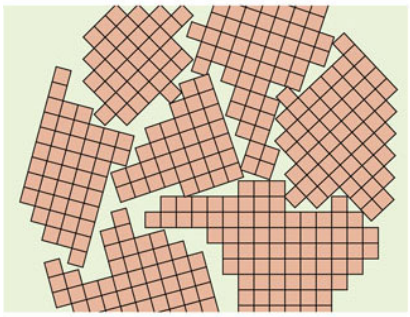
Microstructure – grains from solidification

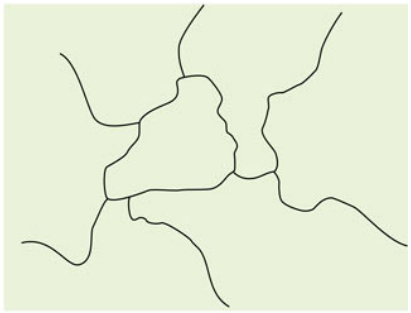
- Single crystals — from a single nucleus

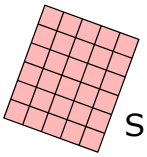




- Polycrystals — from many nuclei

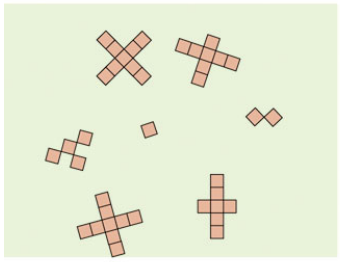




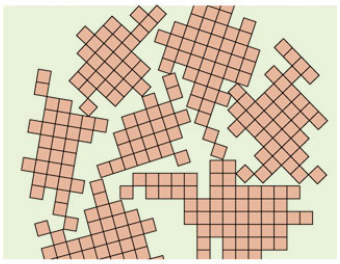


Single crystal

Planar defects
Grain boundaries in polycrystals

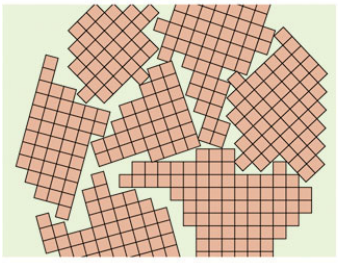


(a)

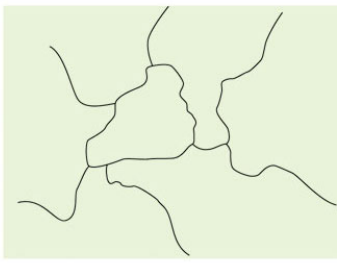


(b)

Nuclei form during solidification in melt



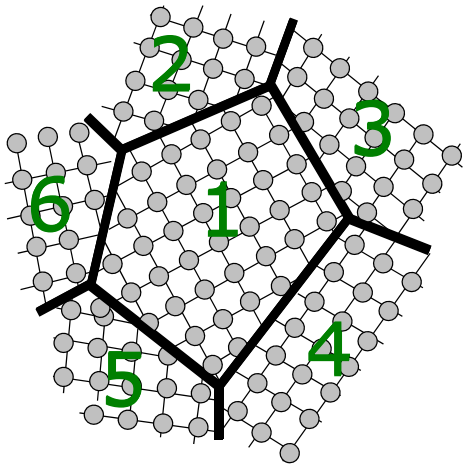
(c)



(d)

Nuclei grow and form grains

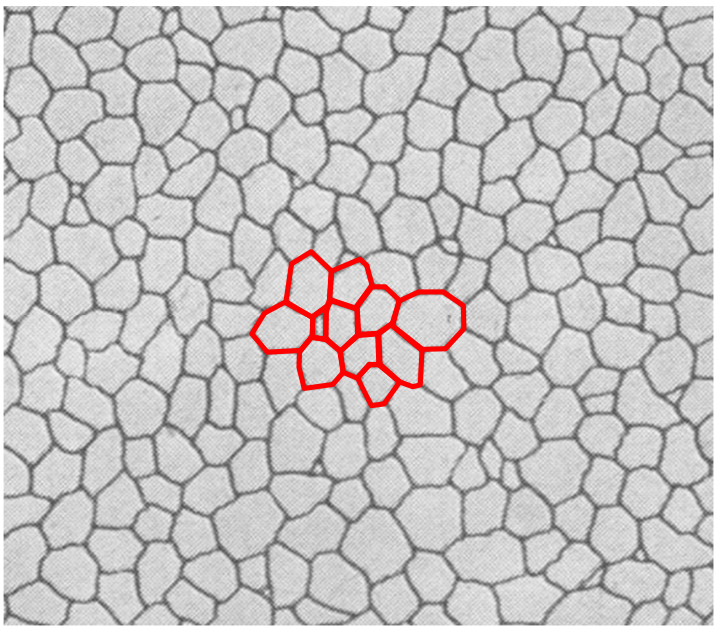
Planar defects
Grain boundaries



Grain boundaries

- Separate two grains i.e. two regions of same crystal structure, but of different crystallographic orientation

Planar defects
Grain boundaries



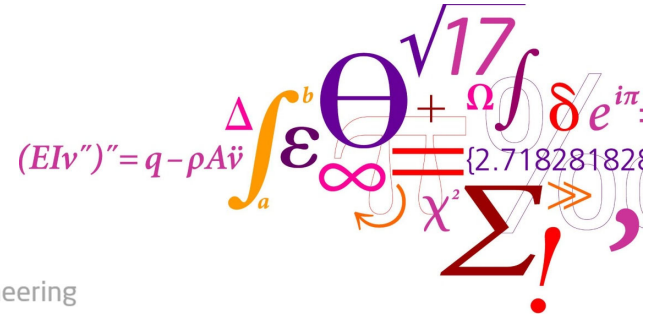
Grain size D

Surface area S
Volume V

Boundary density

$$S_V = \frac{S}{V} \approx \frac{2}{D}$$

Intermezzo
Stacking of close-packed planes



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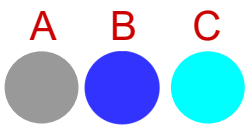
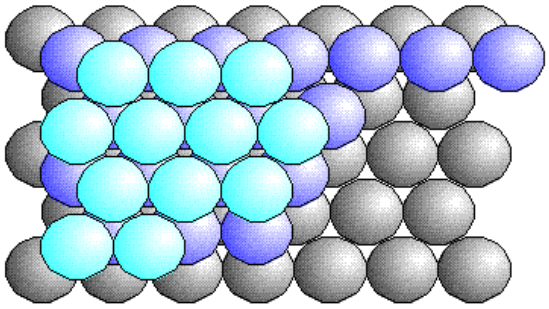
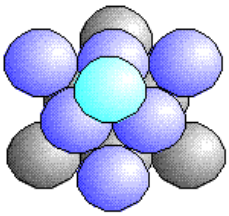
Stacking sequences

fcc stacking sequence

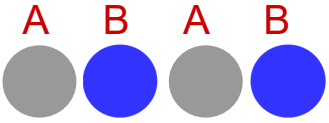


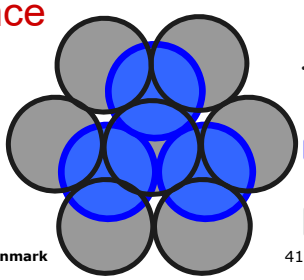


unit cell



hcp stacking sequence





top layer A

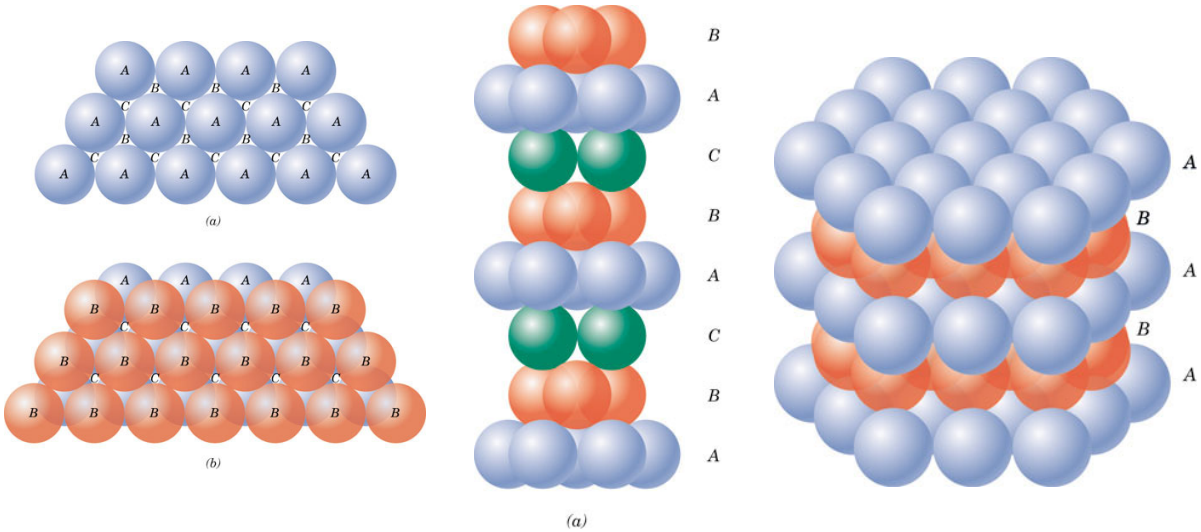
middle layer B

bottom layer A

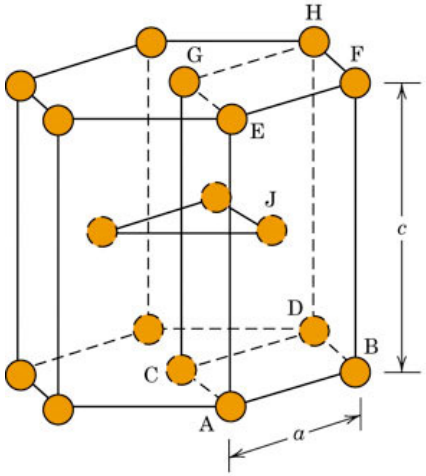
Stacking sequences

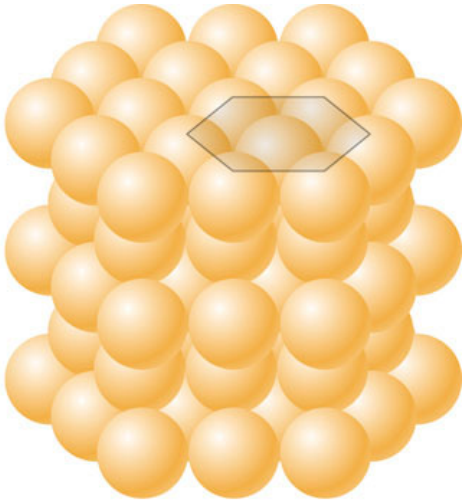
fcc: ABCABCA...

hcp: ABABABA...



Hexagonal close-packed (hcp)





- Atomic packing factor 0.74
- Coordination number 12
- Examples: Mg, Co, Ti

Elements – crystal structures

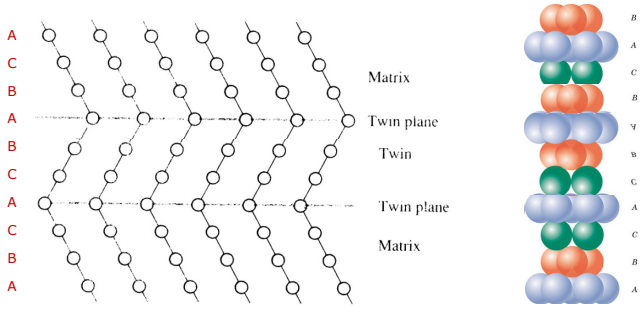
H																	He
Li hcp	Be											B	C cub	N	O	F	Ne
Na hcp	Mg											Al	Si	P	S	Cl	Ar
K	Ca bcc	Sc fcc	Ti bcc	V	Cr	Mn	Fe fcc	Co fcc	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr bcc	Y bcc	Zr bcc	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn ttg	Sb	Te	I	Xe
Cs	Ba	L	Hf bcc	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl bcc	Pb	Bi	Po	At	Rn
Fr	Ra	A	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og

	L	La fcc	Ce fcc	Pr bcc	Nd bcc	Pm bcc	Sm hcp	Eu	Gd bcc	Tb bcc	Dy bcc	Ho	Er	Tm	Yb bcc	Lu
	A	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

	Cubic primitive		Face-centered cubic		Diamond (cubic)
	Body-centered cubic		Hexagonal		Nonmetals

Planar defect
Twin boundaries in polycrystals

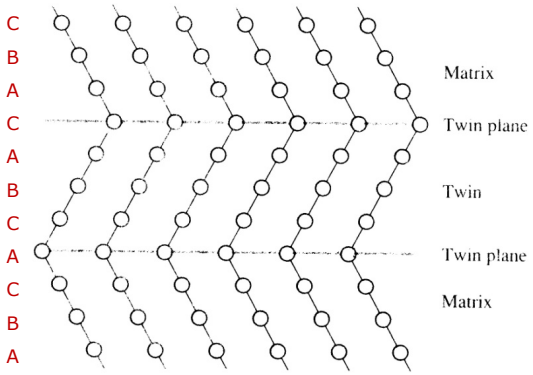
- Twin = mirrored crystalline lattice

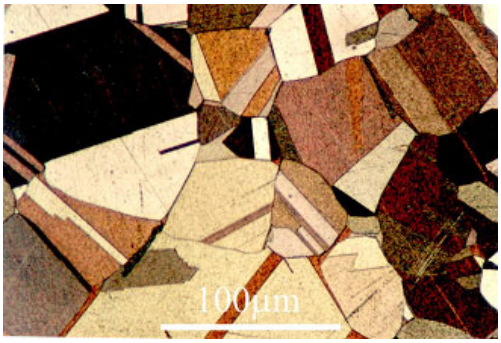


- Coherent boundaries on well-defined lattice planes (fcc {111})
- Twin formation causes shear
- Plastic deformation in non-cubic lattices (”tin cry”)

Planar defects
Twin boundaries

- Twin = mirror symmetry





Cu70-Zn30 wt%, α-phase, annealing twins

Lattice defects

0-dimensional: point defects
vacancies, interstitials, substitutional atoms

1-dimensional: line defects
dislocations

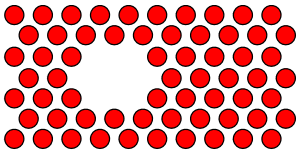
2-dimensional: area (planar) defects
interfaces (stacking faults,
grain-, phase-, twin-boundaries, surfaces)

3-dimensional: volume (bulk) defects
voids, pores, precipitates, inclusions, cracks

Volume defects

Self defects

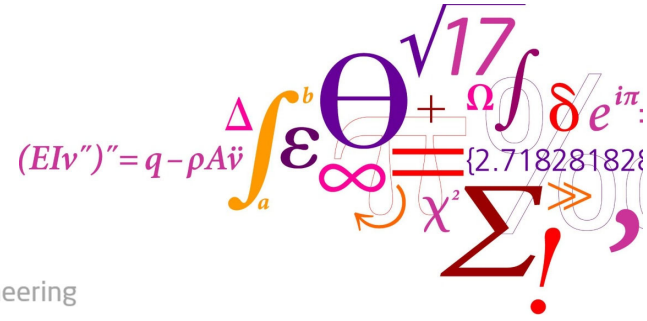
- Clusters of point defects
- Pore = agglomerate of vacancies



- Requires many missing atoms!

Alloys

mixture of two or more elements with metallic bonding



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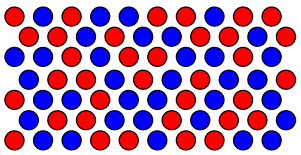
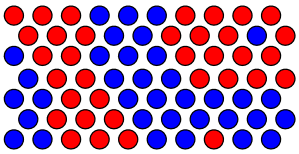
Alloys – three principle types

- Solid solutions = foreign atoms in crystal lattice



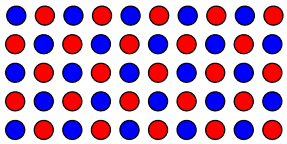
- Atoms unordered in same lattice

- Mixture of different metallic phases



- Distinct phases with different composition and possibly different lattices

- Intermetallic compounds



- Atoms ordered in possibly different lattice

Point defects in alloys

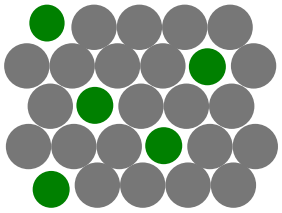
- **Solid solution** = foreign atoms (impurities) in the crystal lattice of host atoms
- **Interstitial** atoms
  ⇒ sitting between lattice sites
  ⇒ interstitial solid solution
- **Substitutional** atoms
  ⇒ substitute atoms on latt. sites
  ⇒ substitutional solid solution
- Crystal structure maintained for solid solutions
- Alternatives – immiscibility
  – intermetallic compounds (new phase of own structure)

Point defects in alloys

Substitutional atoms

substitutional solid solution

(e.g. Ni in Cu)



Hume-Rothery rules

Complete miscibility for substitutional solid solution requires:

- Same crystal structure
- Difference in atomic radius not more than 15%
- Similar electronegativity
- Same valence

Example: Cu and Ni

Otherwise

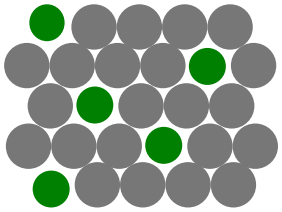
- Partial miscibility
- Immiscibility

Point defects in alloys

Substitutional atoms

substitutional solid solution

(e.g. Ni in Cu)

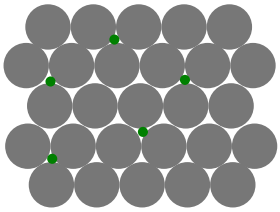


- Foreign atoms on regular lattice sites
- Hume-Rothery rules

Interstitial atoms

interstitial solid solution

(e.g. C in Fe)



- Foreign atoms on interstitial sites
- Only small atoms in holes (as B, C, N, O)

Composition of binary alloys
containing A and B

- Composition *(weight percentage)*
- Proper term: mass fraction

$$C_A = \frac{m_A}{m_A + m_B}$$

$$C_B = \frac{m_B}{m_A + m_B}$$

- Conversion

$$m_A = n_A \mu_A$$

$$C_A = \frac{n_A \mu_A}{n_A \mu_A + n_B \mu_B} = \frac{C_A^* \mu_A}{C_A^* \mu_A + C_B^* \mu_B}$$

- Composition *(atomic percentage)*
- Proper term: amount fraction

$$C_A^* = \frac{n_A}{n_A + n_B}$$

$$C_B^* = \frac{n_B}{n_A + n_B}$$

- Conversion

$$\mu_A = m_A / n_A$$

$$C_A^* = \frac{C_A / \mu_A}{C_A / \mu_A + C_B / \mu_B}$$

m mass
n amount of substance (number of atoms)
μ molar mass (atomic mass, *atomic weight*)

Composition of binary alloys
Applications

- Density

$$\rho = \frac{m}{V} = \frac{m_A + m_B}{V}$$

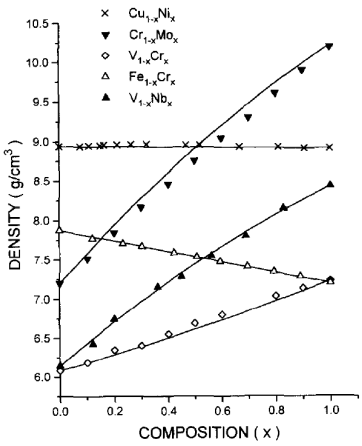
- Naïve estimate: additivity of volumes

$$V = \frac{m_A + m_B}{\rho}$$

$$\approx V_A + V_B$$

$$\approx \frac{m_A}{\rho_A} + \frac{m_B}{\rho_B}$$

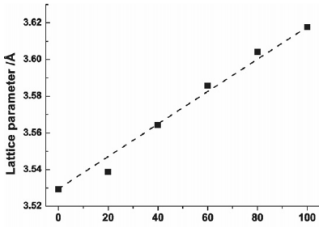
$$\rho \approx \frac{1}{\frac{C_A}{\rho_A} + \frac{C_B}{\rho_B}}$$



- Lattice constant a of solid solutions
  - Vegard's rule

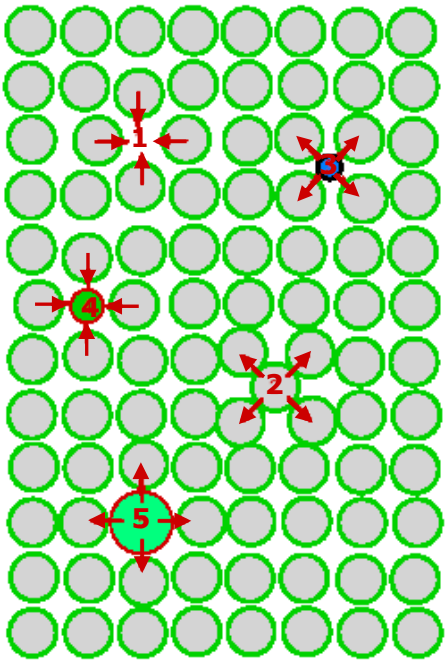
$$a_{ss} = C_A^* a_A + C_B^* a_B$$

  - Limited validity
  - Example CuNi



Ni Cu

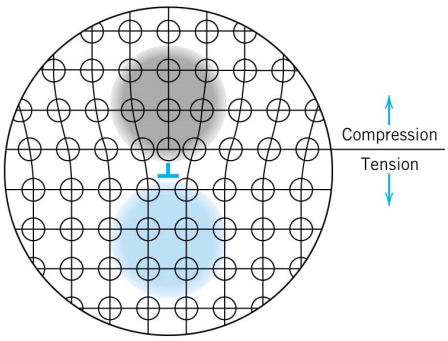
Points defects



- local distortion of the lattice
- interaction
- external stress

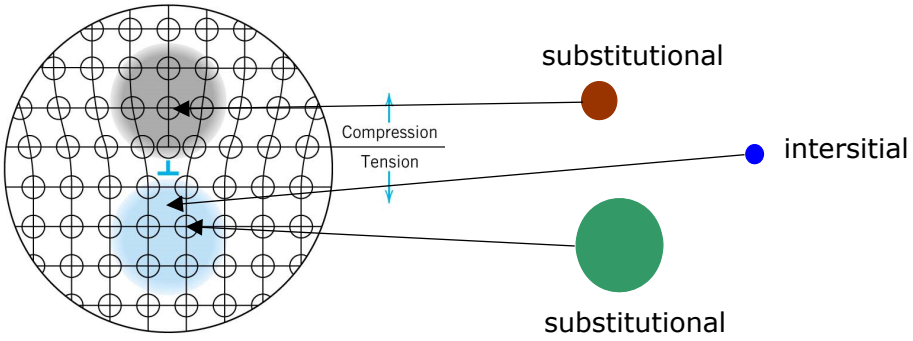
1. Vacancy
2. self-interstitial
3. interstitial impurity
4. small substitutional impurity
5. large substitutional impurity

Interaction: dislocations and point defects



Which position is likely to be occupied by
- an interstitial atom
- a substitutional atom larger than the host ones
- a substitutional atom smaller than the host ones ?

Interaction: dislocations and point defects



Which position is likely to be occupied by
- an interstitial atom
- a substitutional atom larger than the host ones
- a substitutional atom smaller than the host ones ?

Lattice defects

0-dimensional: point defects
vacancies, interstitials, substitutional atoms

1-dimensional: line defects
dislocations

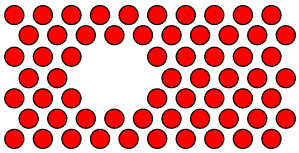
2-dimensional: area (planar) defects
interfaces (stacking faults,
grain-, phase-, twin-boundaries, surfaces)

3-dimensional: volume (bulk) defects
voids, pores, precipitates, inclusions, cracks

Volume defects

Self defects

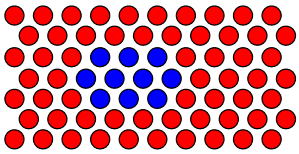
- Clusters of point defects
- Pore = agglomerate of vacancies



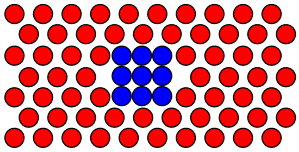
- Requires many missing atoms!

Alien defects

- Particles of second phase
- Precipitates
  - coherent

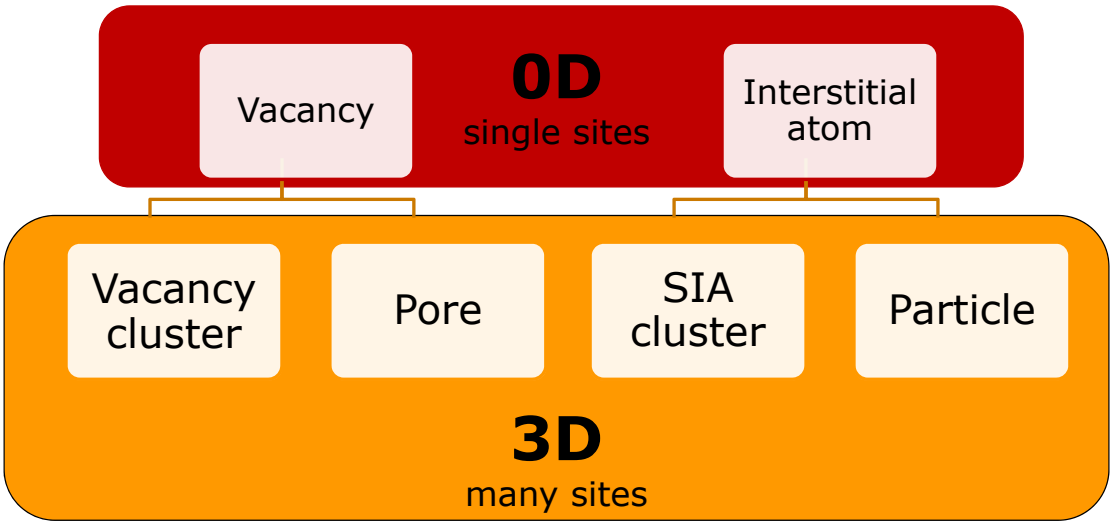


  - incoherent



- Requires many atoms!

Overview



Rôle of defects

- diffusion

- mechanical properties
- electrical properties
- magnetic properties

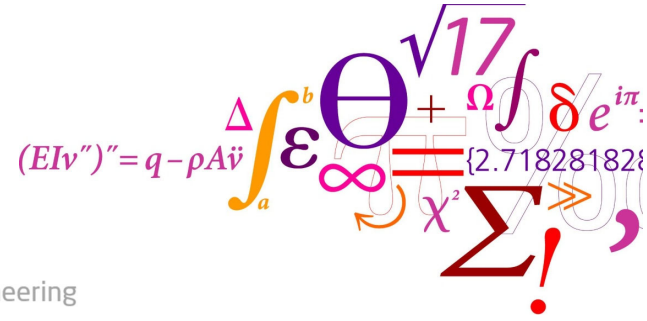
- plastic deformation

- strengthening mechanisms !!!

- various interactions
  e.g. interstitial atoms = obstacles to dislocation movement

Interstitial lattice sites

Where is space for foreign atoms?



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Cubic lattices - comparison

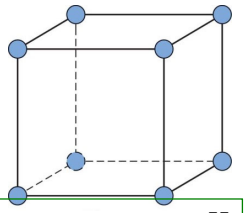
	*	Close-packed direction	Neighbor closest to origin	Atomic dia-meter 2*R*	Atomic packing factor	Coordi-nation number	Examples
sc	1	<100>	[100]*a*	*a*	0.52	6	only α-Po
bcc	2	<111>	[111]*a*/2	$\sqrt{3}a/2$	0.68	8	Cr, W, V, Ta, α-Fe
fcc	4	<110>	[110]*a*/2	$\sqrt{2}a/2$	0.74	12	Al, Cu, Ag, Au, Ni, γ-Fe

* Number of atoms in unit cell Lattice parameter *a*

Random close-packed spheres		0.64		
Ordered close-packed spheres		0.74		

Only fcc is close-packed !

Wanted
Simple cubic lattice

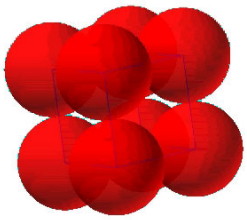


I
- Atoms in unit cell: 1
- Coordination number (# nearest neighbors): 6

III
- Ratio between edge length and atomic radius: $a/R = 2$
- Atomic packing factor: $APF = \pi/6 \approx 0.52$
- Closest packed direction: <100>
- Closest packed planes: {100}
  - ○ Close-packed
  - ☒ Not close-packed

II
- Along edges
  - ☒ Atoms touch each other
  - ○ Atoms do not touch each other
  - – Distance between centers: *a*
  - – Distance between neighbors: 0
- Along face diagonals
  - ○ Atoms touch each other
  - ☒ Atoms do not touch each other
  - – Distance between centers: $\sqrt{2}a$
  - – Distance between neighbors: $\sqrt{2}a - 2R$
- Along volume diagonals
  - ○ Atoms touch each other
  - ☒ Atoms do not touch each other
  - – Distance between centers: $\sqrt{3}a$
  - – Distance between neighbors: $\sqrt{3}a - 2R$

Simple cubic lattice – Interstitial site



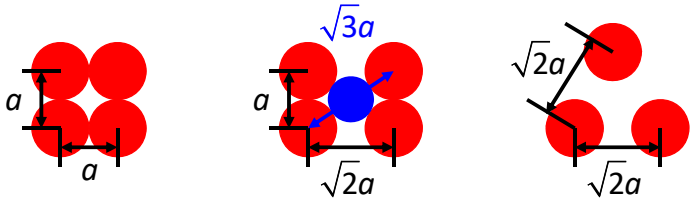
- Hard sphere model
- Interstitial site (hexahedral site)

$$2r_H = \sqrt{3}a - 2R_{at} = 2R_{at}\left(\sqrt{3} - 1\right)$$

$$r_H / R_{at} = 0.73$$

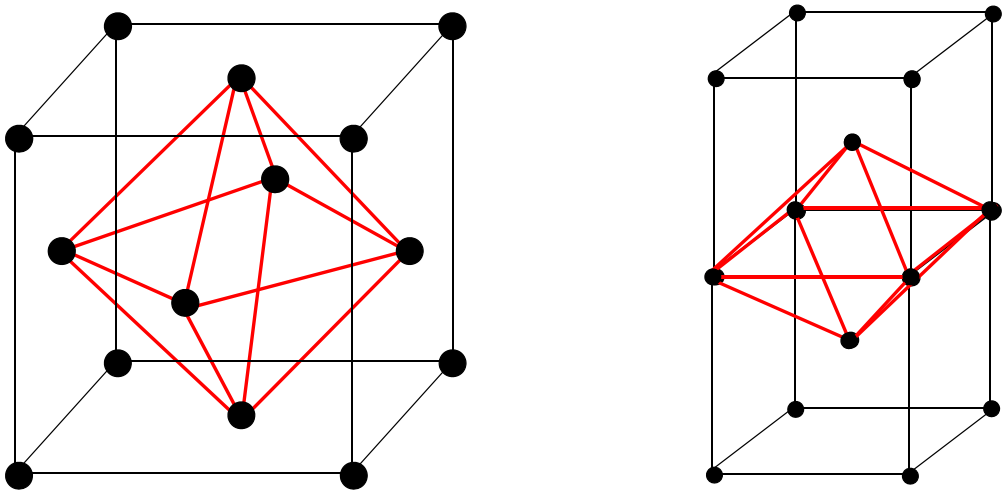
- Crystallographic planes

(100) (110) (111)



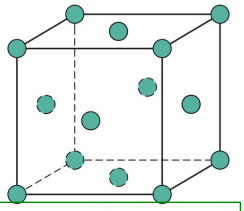
Interstitial sites - octahedral sites

fcc bcc



Radius of interstitial site r
Radius of host atoms R_{at}

Wanted
Face centered cubic lattice



I
- Atoms in unit cell: 4
- Coordination number (# nearest neighbors): 12

III
- Ratio between edge length and atomic radius

$a/R = 4/\sqrt{2}$

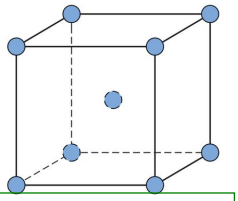
- Atomic packing factor

$$APF = 4\frac{4\pi}{3}\left(\frac{\sqrt{2}}{4}\right)^3 = \frac{\pi\sqrt{2}}{6} \approx 0.74$$

- Closest packed direction: <110>
- Closest packed planes: {111}
  - [x] Close-packed
  - [ ] Not close-packed

II
- Along edges
  - [ ] Atoms touch each other
  - [x] Atoms do not touch each other
    - Distance between centers: a
    - Distance between neighbors: $a - 2R$
- Along face diagonals
  - [x] Atoms touch each other
  - [ ] Atoms do not touch each other
    - Distance between centers: $\sqrt{2}a/2$
    - Distance between neighbors: 0
- Along volume diagonals
  - [ ] Atoms touch each other
  - [x] Atoms do not touch each other
    - Distance between centers: $\sqrt{3}a$
    - Distance between neighbors: $\sqrt{3}a - 2R$

Wanted
Body centered cubic lattice



I
- Atoms in unit cell: 2
- Coordination number (# nearest neighbors): 8

III
- Ratio between edge length and atomic radius

$a/R = 4/\sqrt{3}$

- Atomic packing factor

$$APF = 2\frac{4\pi}{3}\left(\frac{\sqrt{3}}{4}\right)^3 = \frac{\pi\sqrt{3}}{8} \approx 0.68$$

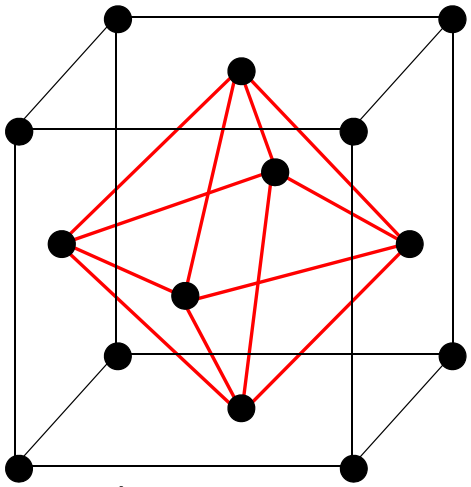
- Closest packed direction: <111>
- Closest packed planes: {110}
  - [ ] Close-packed
  - [x] Not close-packed

II
- Along edges
  - [ ] Atoms touch each other
  - [x] Atoms do not touch each other
    - Distance between centers: a
    - Distance between neighbors: $a - 2R$
- Along face diagonals
  - [ ] Atoms touch each other
  - [x] Atoms do not touch each other
    - Distance between centers: $\sqrt{2}a$
    - Distance between neighbors: $\sqrt{2}a - 2R$
- Along volume diagonals
  - [x] Atoms touch each other
  - [ ] Atoms do not touch each other
    - Distance between centers: $\sqrt{3}a/2$
    - Distance between neighbors: 0

Group exercises

Interstitial sites in fcc

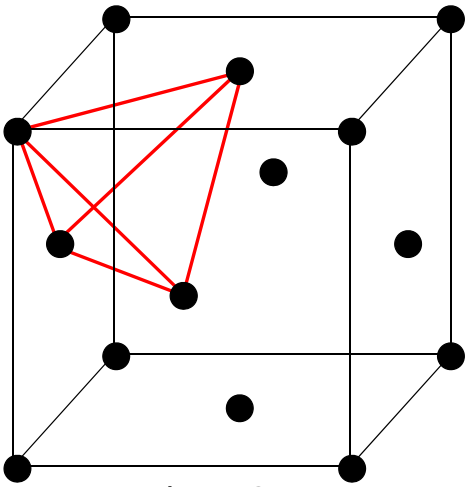
octahedral



number: 4

r_O/R_{at} = 0.414

tetrahedral



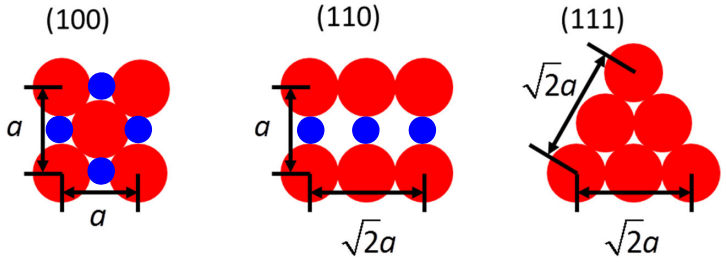
number: 8

r_T/R_{at} = 0.230

Radius of interstitial site r
Radius of host atoms R_{at}

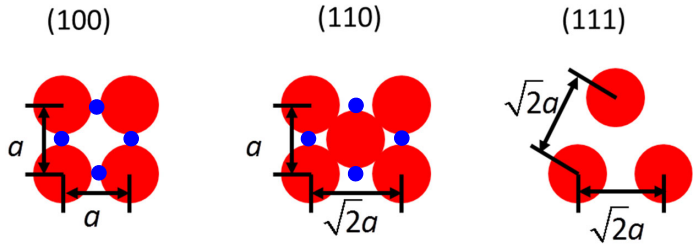
$$a = 2R_{at} + 2r_O \rightarrow r_O = \frac{a}{2} - R_{at}$$

fcc



$$R_{at} = \sqrt{2}a/4$$

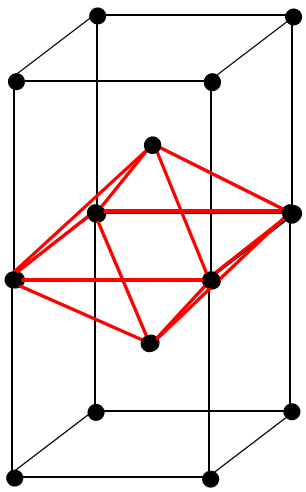
bcc

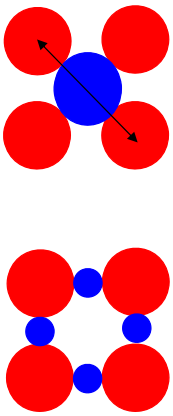


$$R_{at} = \sqrt{3}a/4$$

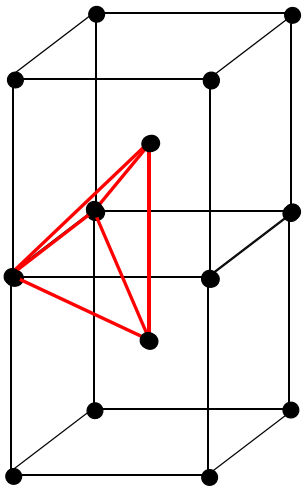
Interstitial sites in bcc

octahedral





tetrahedral



number: 6

r_O/R_{at} = 0.150

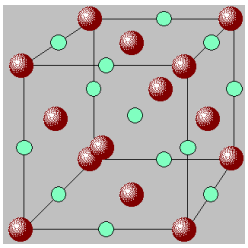
Radius of interstitial site r
Radius of host atoms R

number: 12

r_T/R_{at} = 0.290

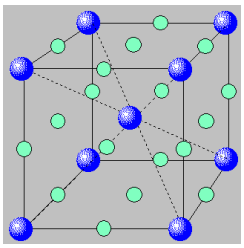
Interstitial lattice sites
Octahedral interstitial sites

- Face-centered cubic



- Number of sites in unit cell 1+12/4 = 4
- Number of atoms in unit cell 4

- Boy-centered cubic



- Number of sites in unit cell 6/2+12/4 = 6
- Number of atoms in unit cell 2

Interstitial lattice sites
Overview

Lattice	Simple cubic	Body-centerd cubic	Face-centered cubic
Atoms in uc	1	2	4
Coordination	6	8	12
APF	52 %	68 %	74 %
Type	Hexahedral	Octahedral	Octahedral
-relative size	0.732	0.150	0.414
-number in uc	1	6	4
Sites/atom	1	3	1