Universidad
Carlos III de Madrid
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MATERIALS SCIENCE AND ENGINEERING

TOPIC 2. STRUCTURE OF MATERIALS III

Topic 2.3:

- Crystalline defects.
- Solid solutions.

PERFECT AND IMPERFECT CRYSTALS

Perfect crystal: All the atoms are in the ideal lattice positions (only true at 0 K).

Real crystal: atoms vibrate

- There positions that are not occupied (vacancies)
- atoms displaced from ideal positions
- There are defects that modify the properties

PERFECT AND IMPERFECT CRYSTALS

Thermodynamics ⇒ Justify ∃ of defects, as $\downarrow \Delta G_{crystal}$

Creation of a defect ⇒ $\Delta H > 0$ and $\Delta S > 0$

Configuration Entropy ⇒ $S = k_B \ln W$

K_B= Boltzmann constant =1.380622 10^{-23} JK^{-1}

W=way of distributing n defects in N possible positions arbitrarily

In 1 mol of C^+ there are N_A possibilities to create 1 vacancy

$W \propto 10^{23}$

$$W = \frac{N!}{(N-n)!n!}$$

Vacancy or defect:

$\Delta H < T\Delta S$

$\Delta G = \Delta H - T\Delta S < 0$

When ↑T ⇒↑ [defects]

DEFECTS TYPES (according to dimensions)

1. Point :

- Vacancies
- Interstitials
- Substitutional
- Schottky
- Frenkel
- Order-Disorder

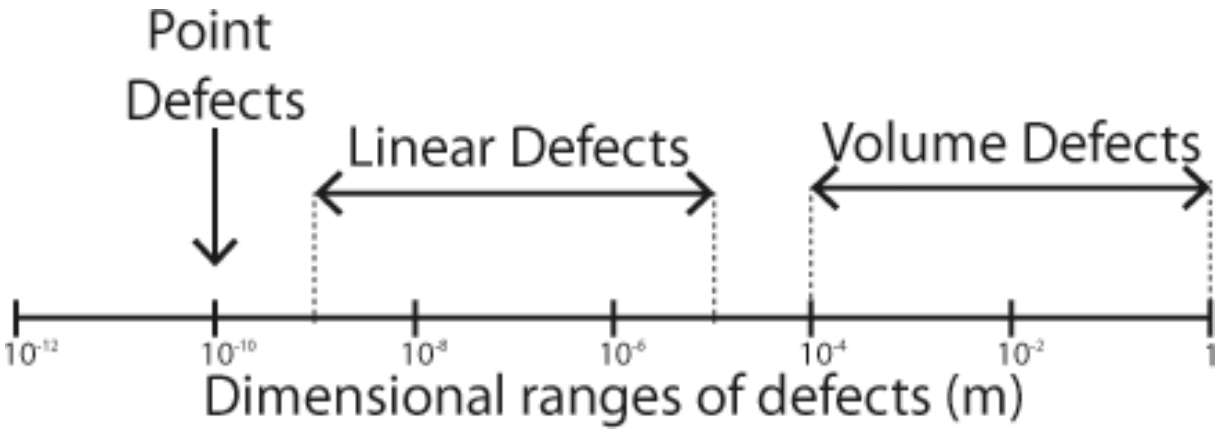
2. Linear: dislocations:

- Edge
- Screw
- Mixed

3. Complex: "clusters"

4. Planar or Extended

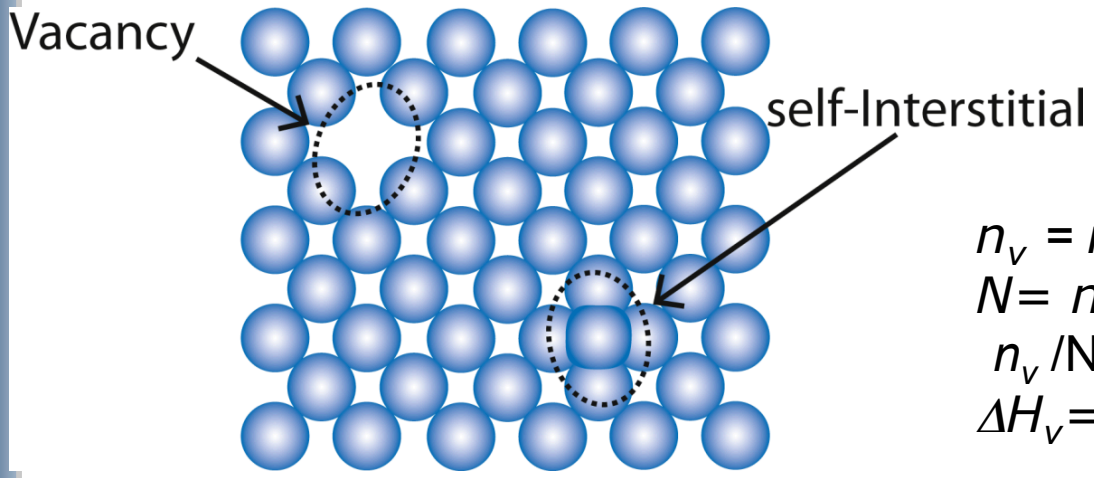
- External Surfaces
- Grain Boundaries
- Twin Boundaries
- Stacking Faults



POINT DEFECTS: VACANCIES AND INTERSTITIALS

Vacancy: When an atom is missing from a position where it should be.

Interstitial: An atom from the crystal occupies the place of an interstitial *(self-interstitial* or *interstitialcy)*



$$n_v = N \exp\left(\frac{-\Delta H_v}{RT}\right)$$

n_v = nº *vacancies per cm³*
N= nº of lattice points per cm³
n_v /N = fraction of *vacancies*
ΔH_v= *Formation energy (J.mol^{-1})*

vacancies concentration at equilibrium $\frac{N_v}{N} \approx 10^{-4}$ max

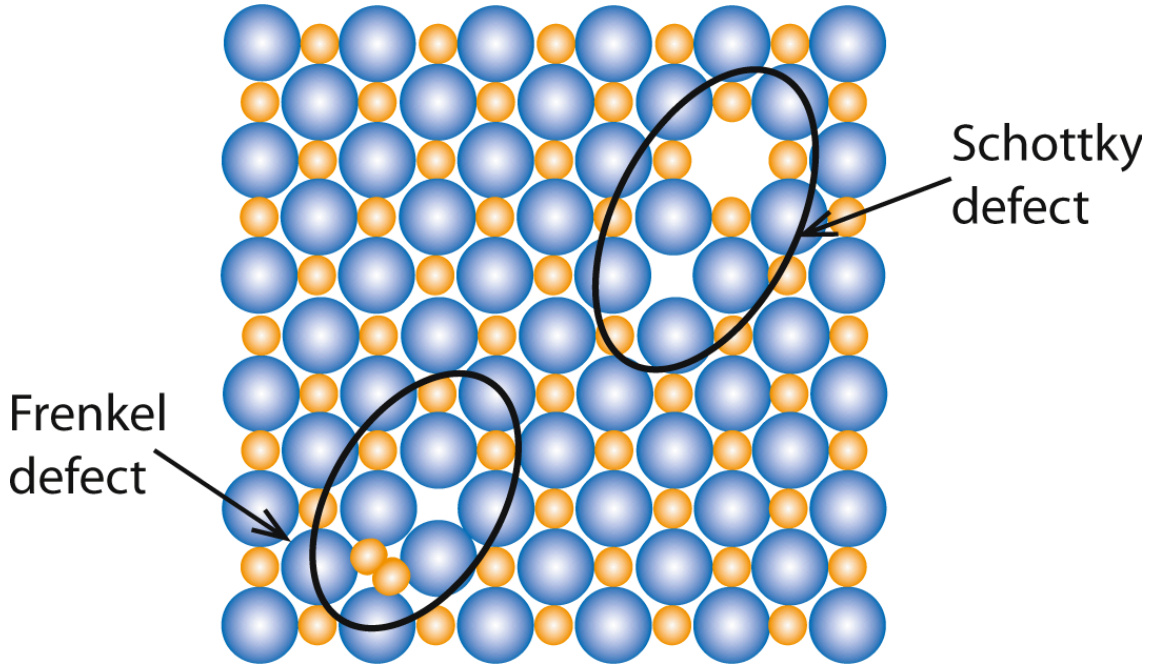
They are produced : ⇒ during solidification (impurities, alloys)
⇒ by particle bombardment with ↑E
⇒ during plastic deformation (processing)
⇒ when ↑T ⇒ ↑thermal vibrations ⇒ ↑n_v

POINT DEFECTS: SCHOTTKY AND FRENKEL

DEFECTS IN **IONIC CRYSTALS**

Schottky Defect: Vacancy in an ionic crystal.
In order to maintain neutrality ⇒ Anionic and cationic vacancies appear

Frenkel Defect: migration of an ion from its normal position to an interstitial position (combination vacancy-interstitial)



POINT DEFECTS: SCHOTTKY AND FRENKEL

Nº of Schottky defects: n_s

$$n_s = N \exp(-\frac{\Delta H_s}{2RT})$$

Nº of Frenkel defects : n_F

$$n_F = \sqrt{NN_i} \exp(-\frac{\Delta H_F}{2RT})$$

ΔH_S = E for Schottky defect creation
ΔH_F= E for Frenkel defect creation
N= nº of lattice positions
N_i= nº of interstitial positions
T= Temperature (K)

In a crystal $\Delta H_S \neq \Delta H_F \Rightarrow$ the defect with the lowest ΔH will form

nº defects increases with temperature

POINT DEFECTS: SCHOTTKY AND FRENKEL

	Compound	*ΔH (eV)*	*ΔH (10^{-19} J)*
Schottky defects	MgO	10.57	6.60
	CaO	9.77	6.10
	LiF	3.75	2.34
	LiCl	3.40	2.12
	NaCl	3.69	2.30
	KCl	3.62	2.26
Frenkel defects	ZrO_2	6.57	4.10
	CaF_2	4.49	2.80
	SrF_2	1.12	0.70
	AgCl	2.56	1.60
	AgBr	1.92	1.20

NaCl (T_f=801 ºC) ΔH_s= 3.69x10^{-19} J
T=300K n_s= 2.64x10^{4} vacancies/mol
T=1000K n_s= 9.38x10^{17} vacancies/mol

MgO ΔH_s= 10.57x10^{-19} J
T=300K n_s= 2.12x10^{-32} vacancies/mol
T=1000K n_s= 1.39x10^{7} vacancies/mol

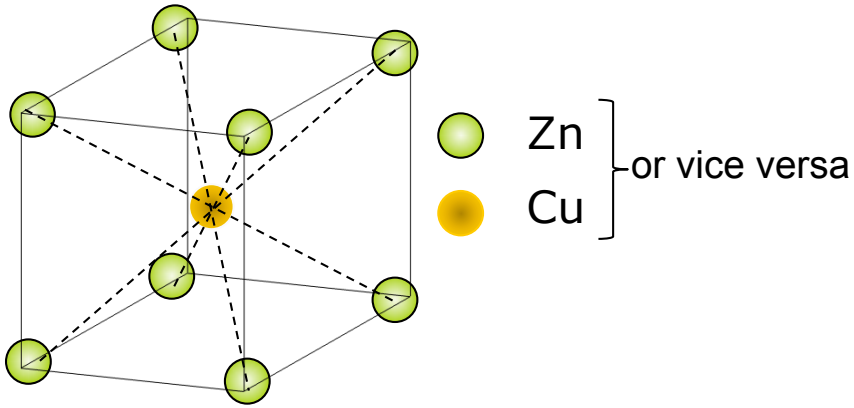
$\Delta H_s(MgO) > \Delta H_s(NaCl)$
$\Rightarrow n_s$ low, more difficult to create vacancies.

POINT DEFECTS: ORDER-DISORDER IN SOLID SOLUTIONS

Order-disorder phenomena (in substitutional solid solutions):
Atoms of one sub-lattice occupy positions corresponding to the other and vice versa (metallic alloys). *Solids with elements that have similar electronegativity*

450 ºC

β' ⇄ Cu/Zn β (bcc)



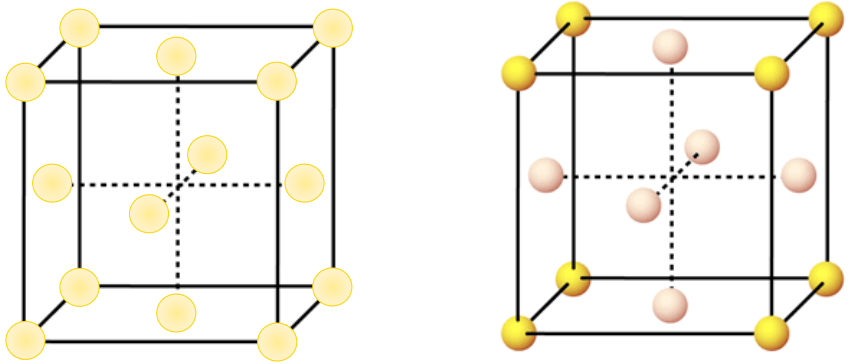
Brass β´ (ordered)

T>390 ºC

Disordered

T<390 ºC

Ordered



Cu-Au Alloys

Brass β': Cu centre Zn corners

Brass β: Cu and Zn arbitrarily distributed in BCC

LINEAR DEFECTS : DISLOCATIONS

DISLOCATIONS

They are defects that produce distortion in the lattice situated around a line.

Characteristics: they can be displaced in the interior of a crystal by applying relatively low forces and can produce a complete displacement over crystalline planes.

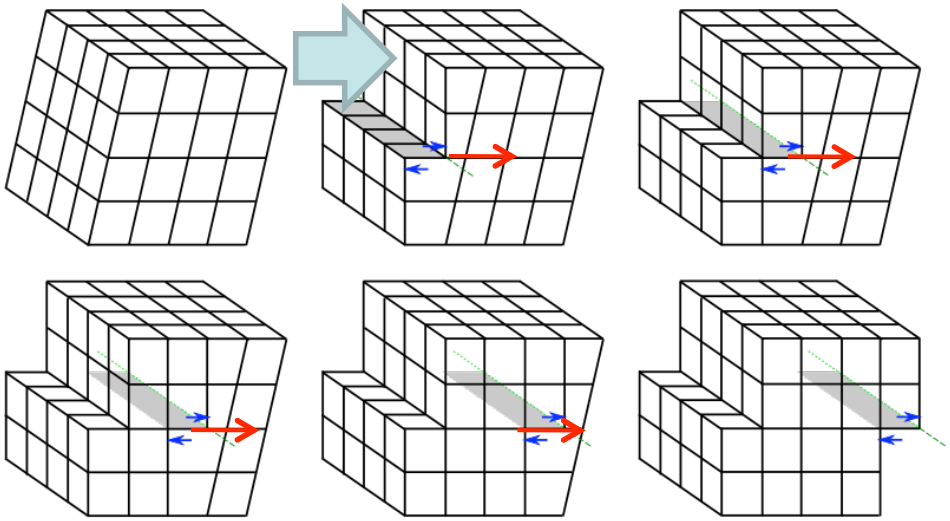
Explain: - $E_{theoretical}$ (Young modulus) > $E_{experimental}$
- Plastic deformation in metals (workability, ductility)

Formation:
- during solidification
- through plastic or permanent deformation of crystal
- through concentration of vacancies
- through atomic disarrangements in solid solutions

Types:
- edge dislocation, or Taylor dislocation
- screw dislocation, or Burgers dislocation
- mixed dislocation

EDGE DISLOCATIONS (or TAYLOR)

⇒ Geometric modification of the lattice: equivalent to an extra plane of atoms ⇒ Energetic modification (they store energy)



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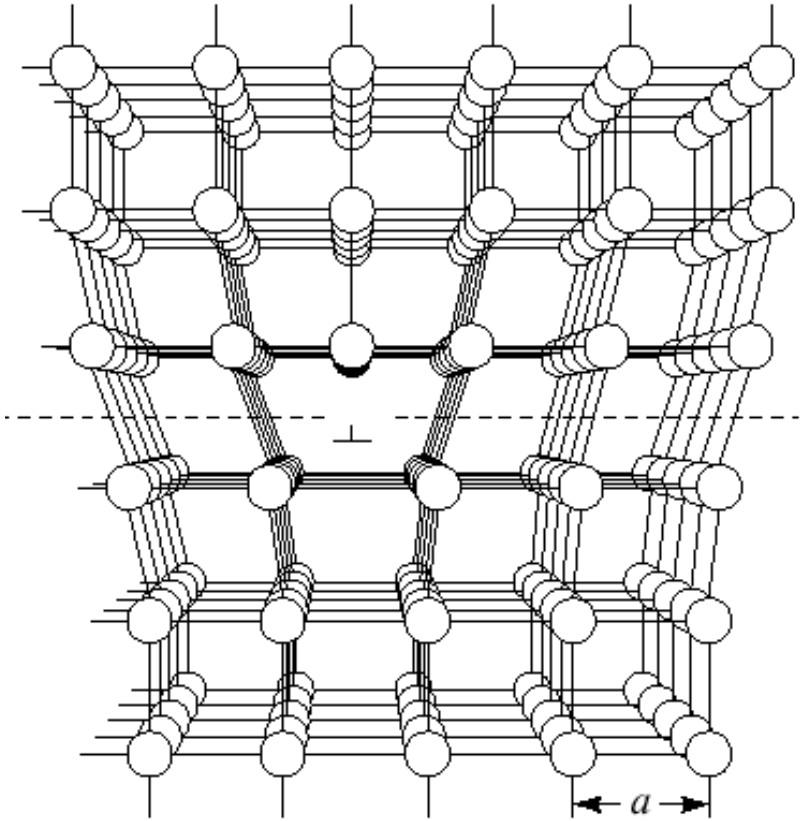


Dislocation line.- ⊥ point A
Slipping plane.- line of points

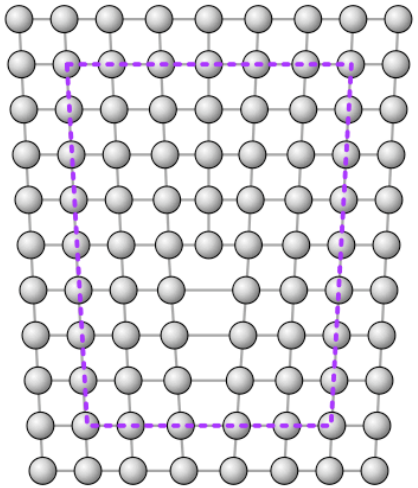
William D. Callister, Jr., Materials Science and Engineering : An Introduction, John Wiley & Sons, Inc.

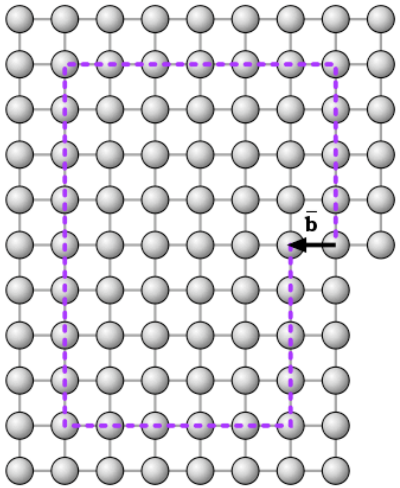
EDGE DISLOCATIONS (or TAYLOR)

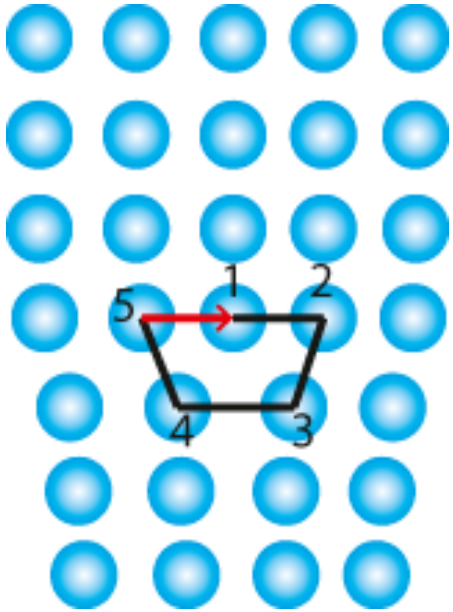
* Dislocation characterization: Burgers Vector (b)

Burgers Vector: magnitude and direction of the lattice distortion associated with the dislocation

Magnitude: distance 1-5
Direction: 1-5 or 5-1
b ⊥ to dislocation line
b || to the direction movement



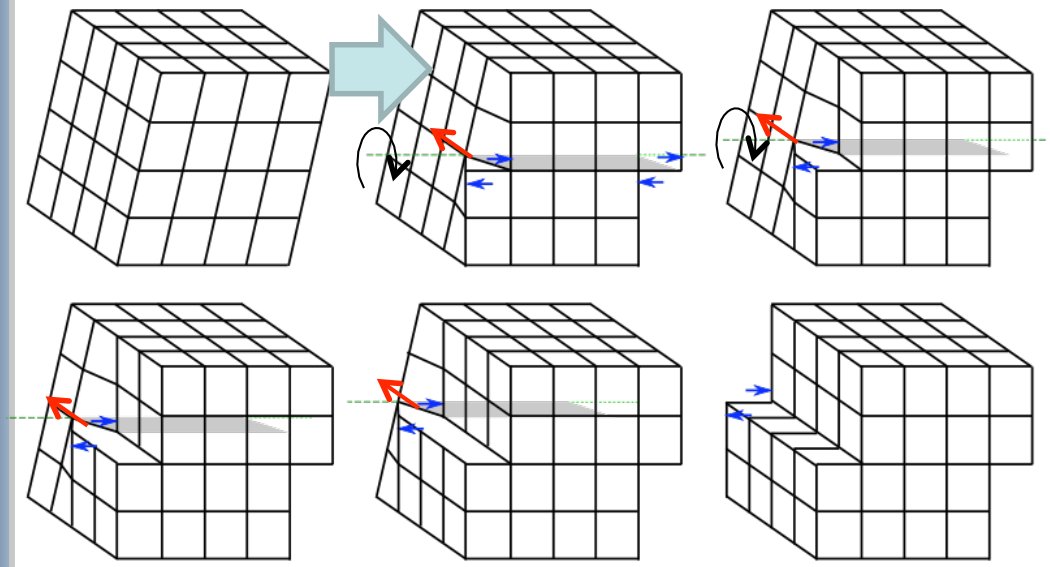




SCREW DISLOCATIONS (or BURGER)

⇨ Locally curves some atom lines.

The effect is as if a shear stress is applied to produce a distortion



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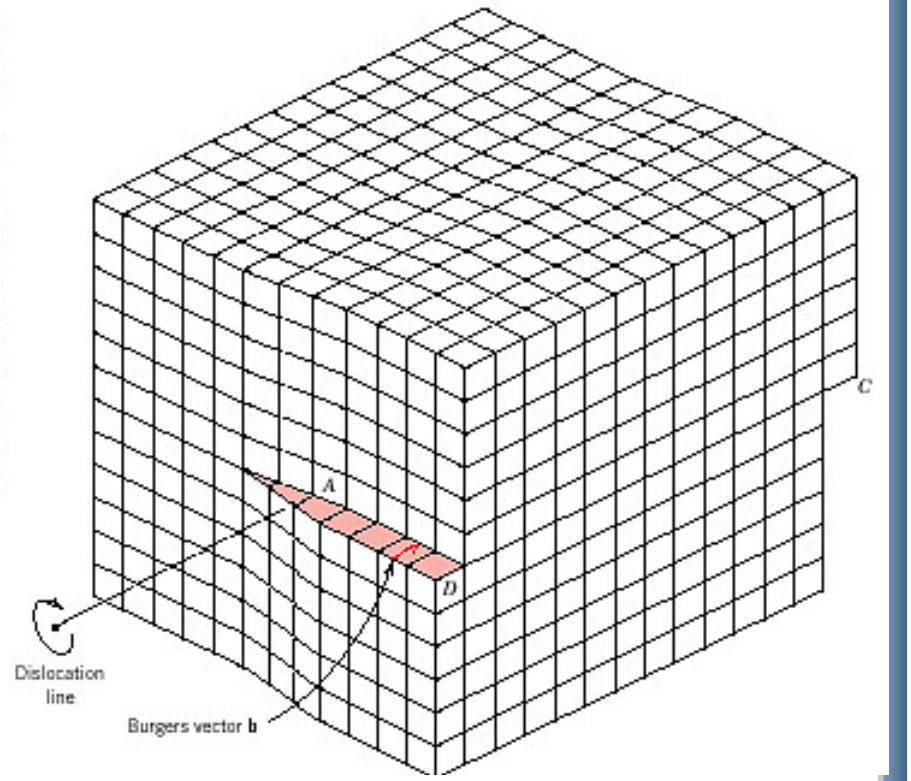


We can move from the inferior to the superior plane through the dislocation line.

William D. Callister, Jr., Materials Science and Engineering : An Introduction, John Wiley & Sons, Inc.

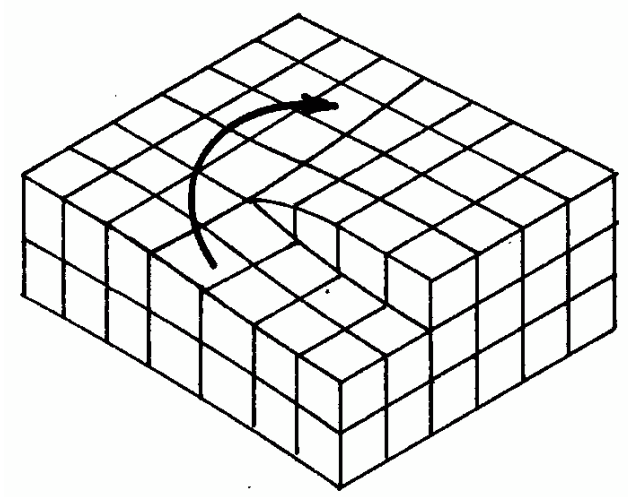
SCREW DISLOCATIONS (or BURGER)

* Burgers Vectors in screw dislocations:

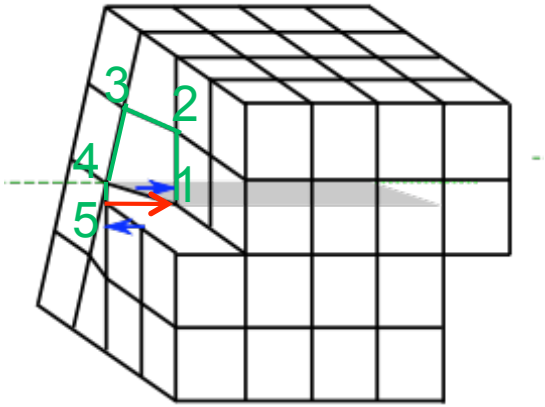
The magnitude and distance from 1-5 define **b**

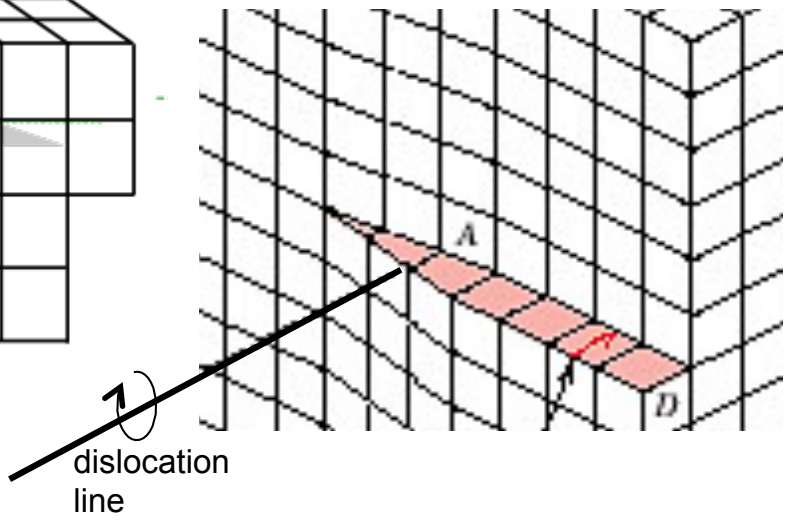
b || to dislocation line SS´

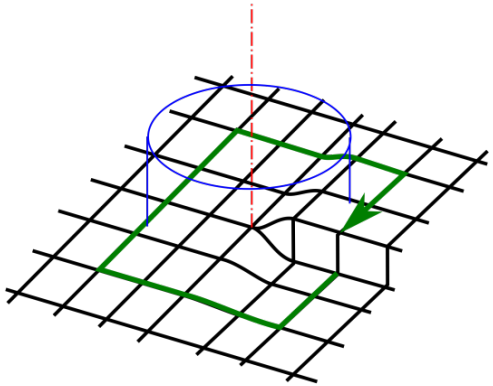
b ⊥ to the direction of movement



We can trace a screw (spiral ramp) around the dislocation.







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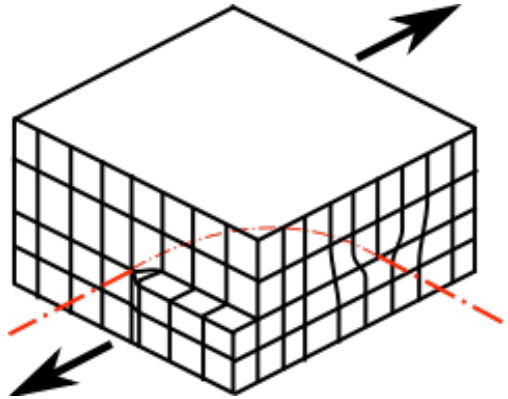
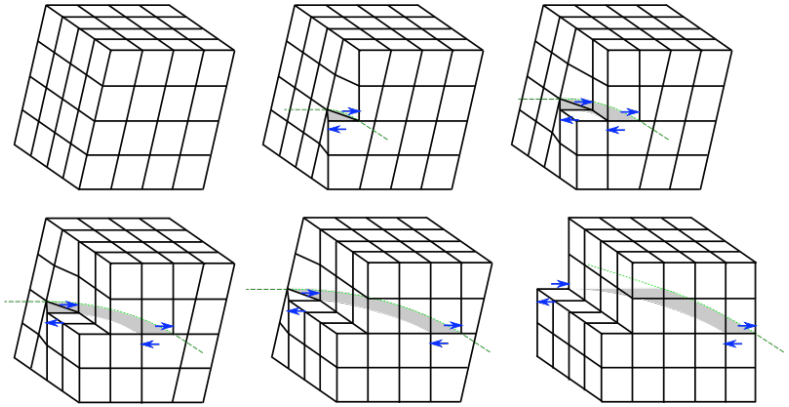
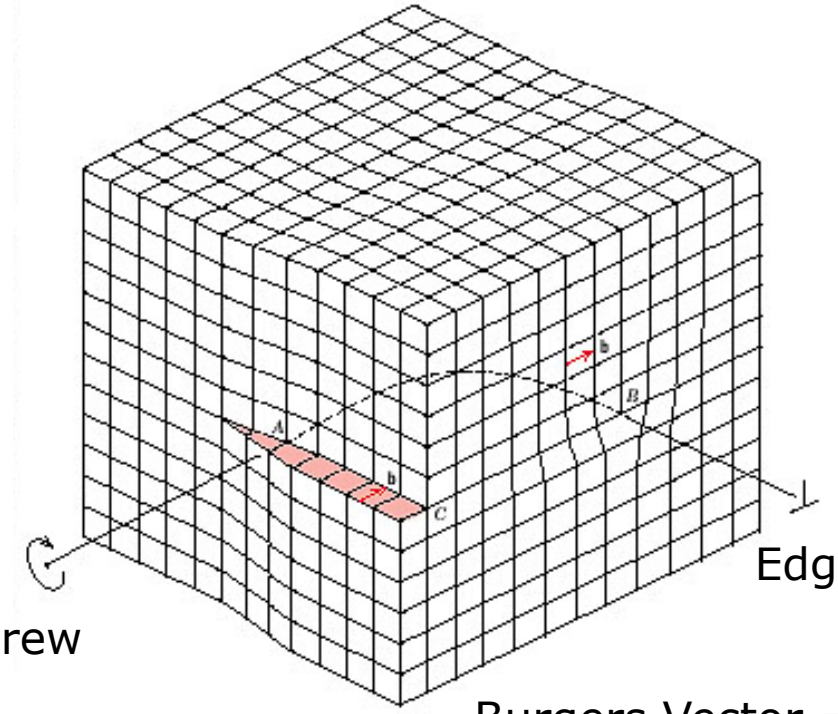
MIXED DISLOCATIONS

If there are many dislocations ⇒ they are mixed (**MIXED dislocations**)







The Burgers vector will be the same at all points along its line even though the dislocation might change direction and nature within a crystal.

http://commons.wikimedia.org/wiki/File:Dislocation_mixte_perspective_iso.svg
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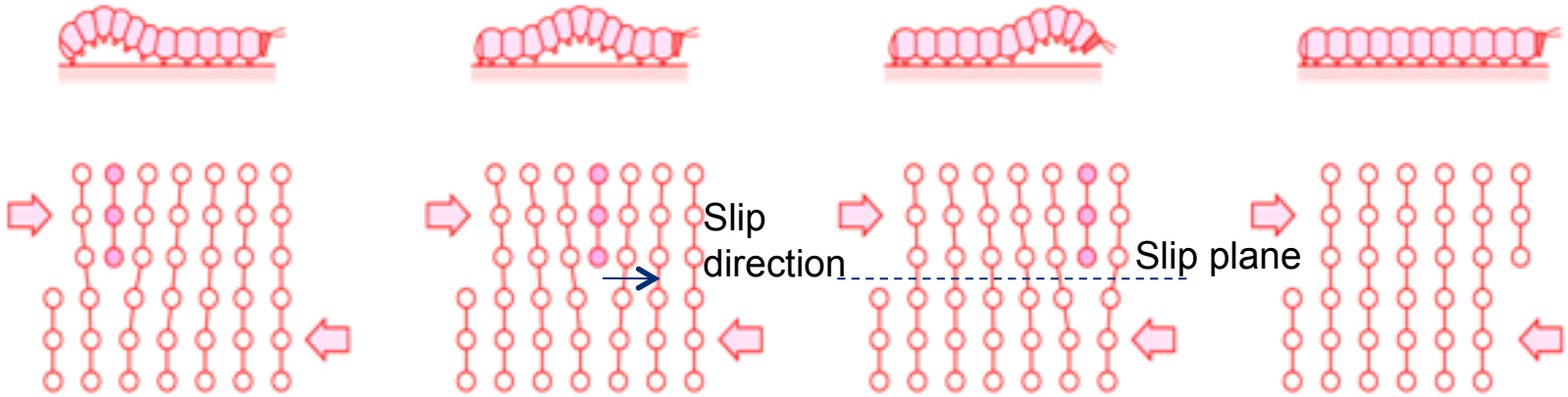
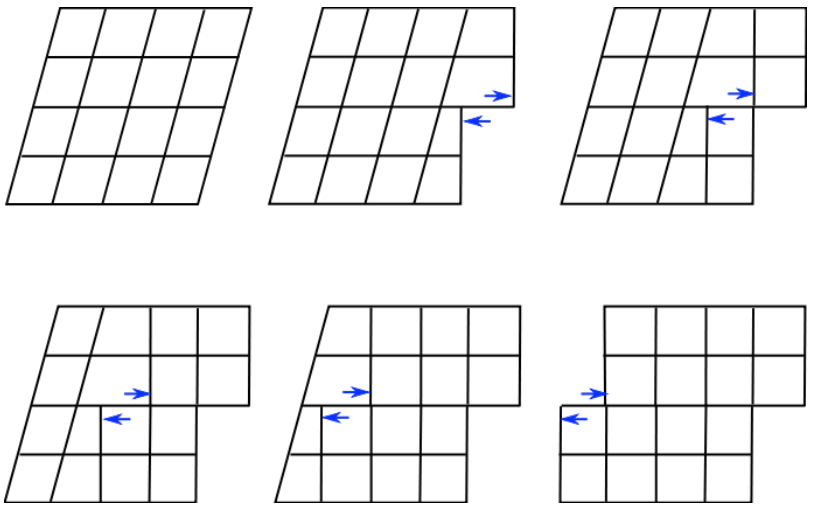
William D. Callister, Jr., Materials Science and Engineering : An Introduction, John Wiley & Sons, Inc.

DISLOCATIONS MOVEMENT

Dislocation movement (edge and screw) when a shear stress is applied





slip direction: the direction in which the dislocation moves

slip plane: the plane in which the dislocation moves

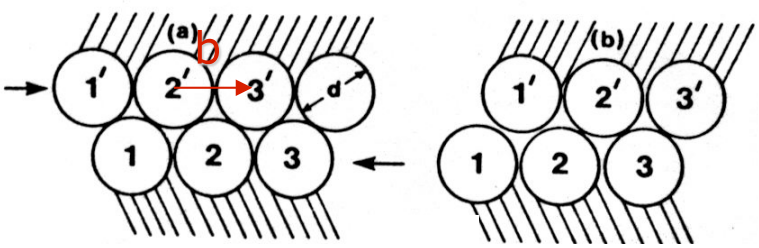
The combination of the slip direction and the slip plane is the **slip system**

PLASTIC DEFORMATION : SLIPPING OF DISLOCATIONS

Dislocations movement parallel to the directions of maximum packing ⇨ Lower distance between them ⇨ + easy sliping

E used to move a dislocation= $E \propto |b|^2$

Compact Direction

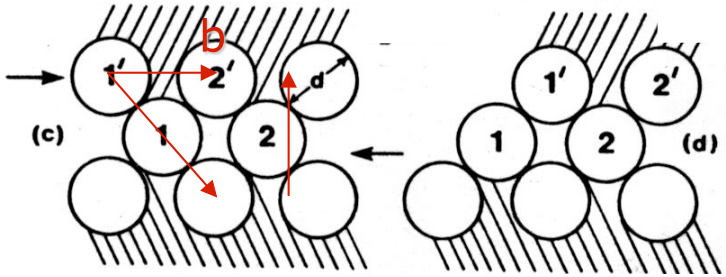


For metallic materials, the burgers vector for a dislocation will be the magnitude equal to the interatomic spacing.

$$|b| = 2R$$

$$E_b \propto 4R^2$$

NON Compact Direction



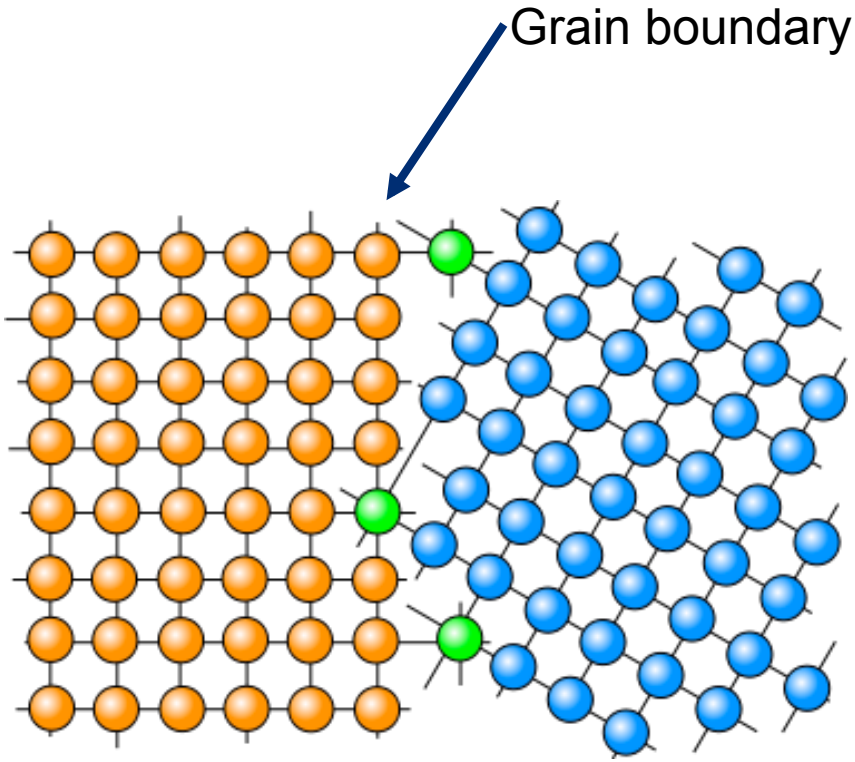
A.R. West. "Solid State Chemistry and its applications". Wiley.Chichester,1992

$$b^2 + b^2 = (4R)^2 \Rightarrow b = 2\sqrt{2}\cdot R$$

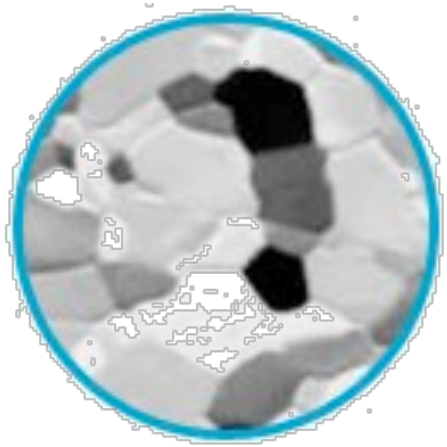
$$E_b \propto 8R^2$$

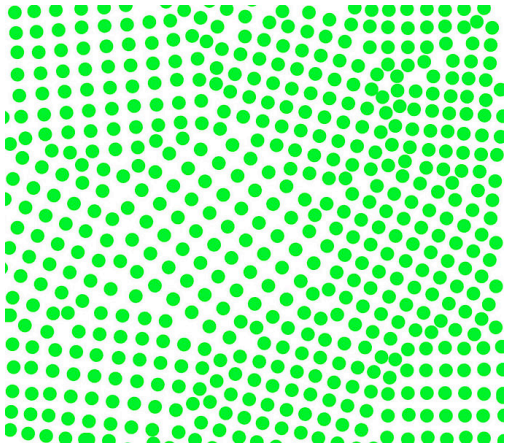
PLANAR DEFECTS: GRAIN BOUNDARIES

They separate crystals with different orientation .
Formation: during solidification: ≠ crystals are formed when ≠ nuclei grow simultaneously.



http://commons.wikimedia.org/wiki/File:Joint_de_grain_reseau_coincidence.svg



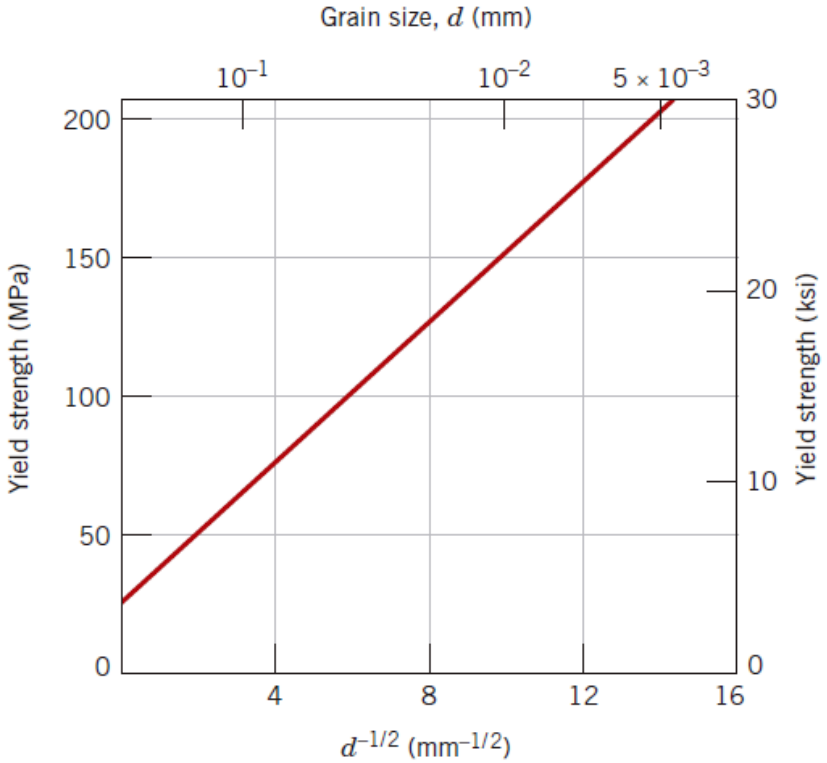


They limit dislocations movement in the material

PLANAR DEFECTS : GRAIN BOUNDARIES

Boundary width: 2-5 interatomic distances
Very <u>energetic</u> zones (atomic packing < less than in interior):
- Solid state reactions
-↑ Atomic diffusion

Materials properties = f (grain size)



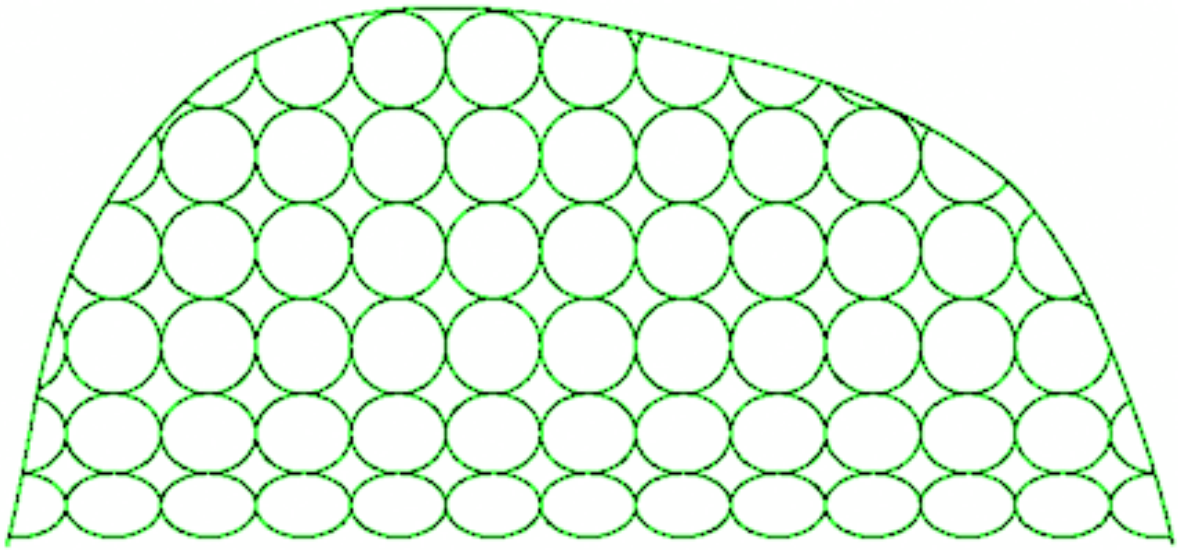
When grain size ↓
⇒Mechanical resistance↑
Dislocation movement is limited when there are many grain boundaries.

William D. Callister, Jr., Materials Science and Engineering : An Introduction, John Wiley & Sons, Inc.

PLANAR DEFECTS: EXTERNAL SURFACES

EXTERNAL SURFACE

It is the end of the crystal or grain structure
Coordination numbers at the surface < at the interior of the crystal ⇒
$E_{surface} > E_{interior}$



PLANAR DEFECTS : STACKING FAULTS

STACKING FAULTS

In fcc and hcp structures

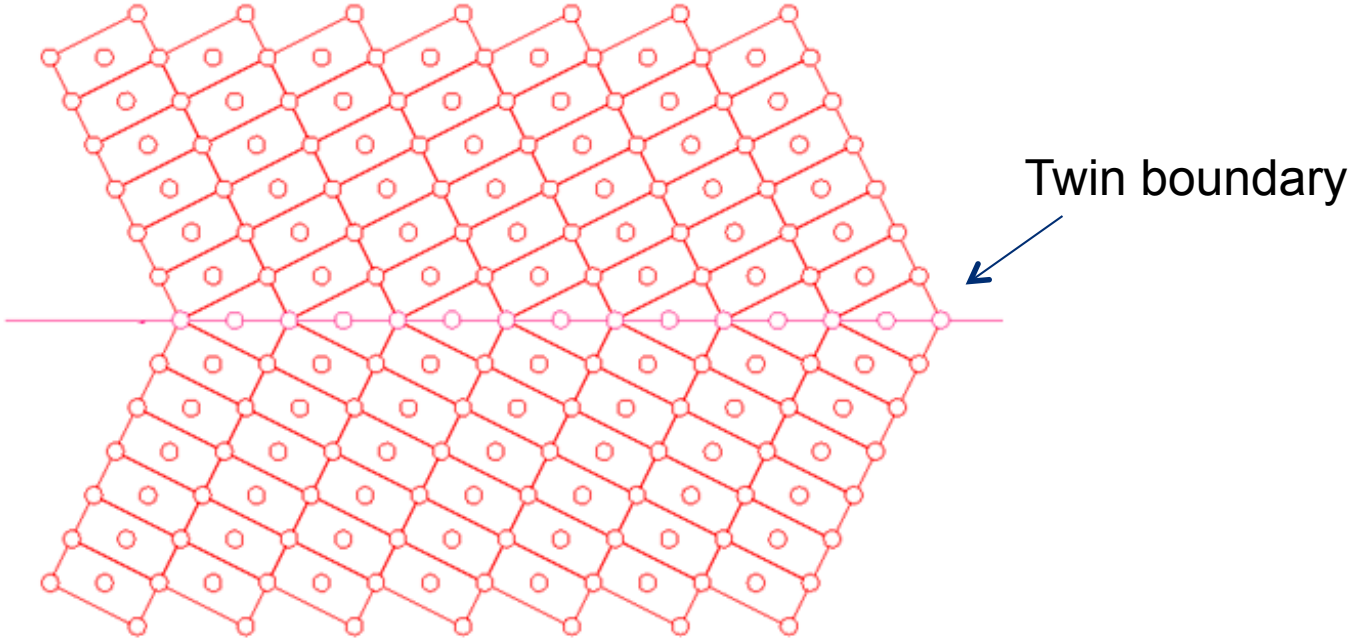
	hcp	fcc
perfect lattice :	...ABABAB...	...ABCABCABC...
Stacking fault:	...ABABCAB...	...ABCABABC...

PLANAR DEFECTS : TWIN BOUNDARIES

Twin boundary:
Boundary that separates two parts of a crystal with a small difference in the orientation (misorientation) of the planes (crystal twinning). Highly symmetrical interface, often with one crystal the mirror image of the other

Formation: Deformation process or during thermal treatments

*Produce ↑ mechanical resistance ⇒ make difficult dislocation gliding



PLANAR DEFECTS: TWIN BOUNDARIES

Brass (70 Cu / 30 Zn)

SOLID SOLUTION

When we add another element to a material in the liquid state

Formation of a SOLID SOLUTION

Def. *"Solid that has 2 or more elements dispersed as atoms in a structure that has only one phase "*

"Phase of variable composition"

SUBSTITUTIONAL solute or impurity atoms replace or substitute the host atoms

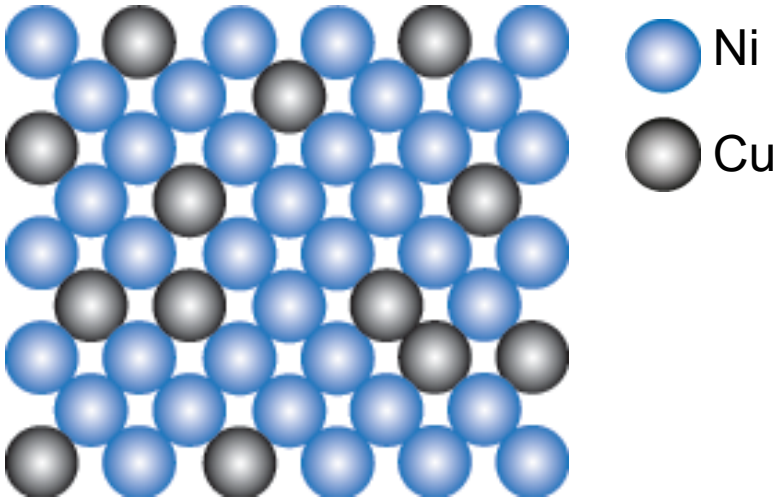
INTERSTITIAL, elements with small radius in octahedral or tetrahedral sites (H, C, N, B y N)

FORMATION of a new PHASE

SOLID SOLUTION

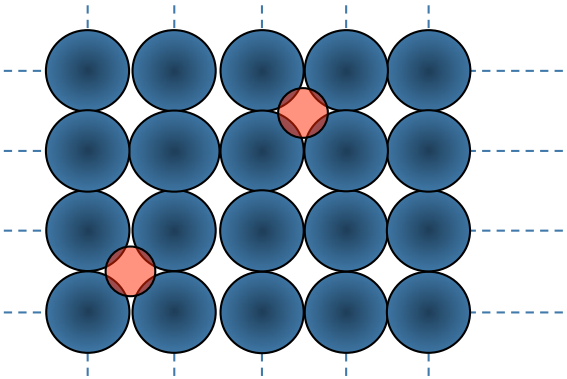
A) Substitutional solid solution

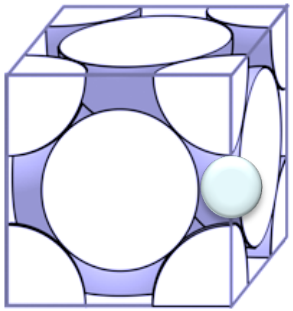
$T > T_f$ during cooling
70g Cu (fcc) + 30 g Ni (fcc) in liquid state → new structure with **a** intermediate between Cu and Ni

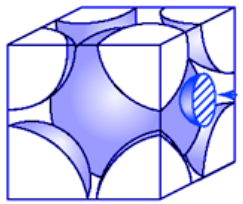


B) Interstitial solid solution

Small atoms located in octahedral sites or tetrahedral sites







SOLID SOLUTION : HUME-ROTHERY RULES

Hume-Rothery rules for the formation of substitutional solid solutions :

1) The same crystal structure
2) Atoms or ions with **similar radius**
   - For ceramics difference < 30%
   - For metals difference < 15%
   - For differences > 15% limited solubility (<1%)
5) They must have similar **electronegativities**
6) **Valance**: In ceramics: They must have the same valance.

If all conditions are fulfilled ⇒ we do not necessarily have total solubility_

-If one or more conditions are not fulfilled ⇒ partial solubility