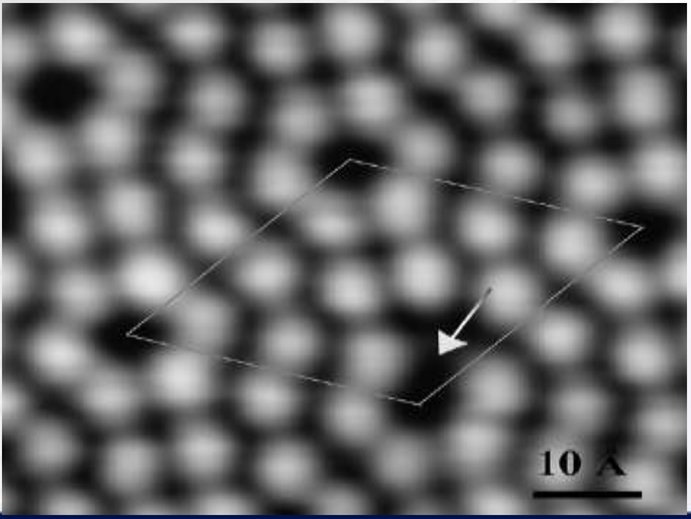
UNESA



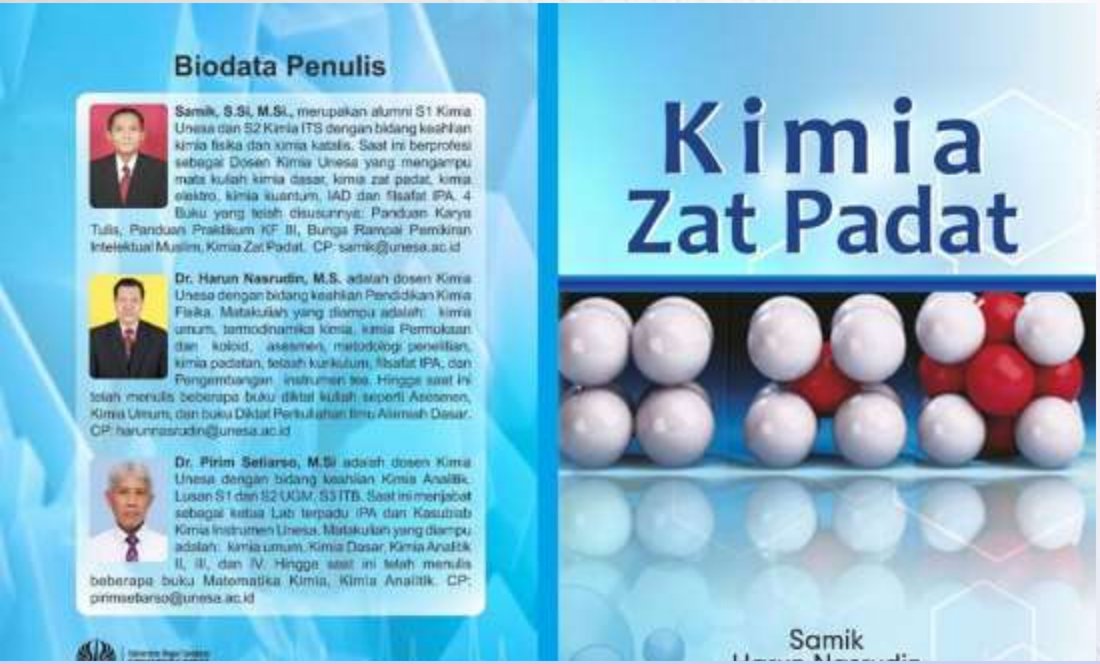
CACAT KRISTAL, SENYAWA NONSTOIKIOMETRIK, DAN LARUTAN PADAT

Oleh

Dr. H. Harun Nasrudin, M.S.

Samik, S.Si., M.Si.

Untuk lebih memahami materi ini silahkan baca Bab VI di buku kami / yg lain:



PPT ini digunakan untuk mempermudah pembelajaran, kebanyakan saya ambil dari berbagai literatur buku dan PPT (terutama yg berbahasa Inggris) dan dari buku Kimia Zat

Mau ebook buku Kimia Zat Padat, silahkan klik https://bit.ly/ebukuKZP / 085731160005

OVERVIEW

DEFINITION & Classification of Defects

solid solution

nonstoikiometri

- **Point defects: solute atoms (strength, conductivity)**
- **Line defects: dislocations (plastic deformation)**
- **Surface defects: external surface (crystal shape)**
- **Volume defects: voids, inclusions (fracture)**

- Struktur kristal sempurna, partikelnya disusun secara berulang dan teratur, mengulangi pola tiga dimensi
- Fakta: susunan partikel penyusun kebanyakan bahan kristal di alam / dibuat di laboratorium adalah tidak sempurna / cacat.
- Berdasarkan dimensinya, terdapat 4 jenis cacat kristal yaitu cacat titik, cacat garis, cacat bidang, dan cacat ruang.
- Senyawa non-stoikiometrik = senyawa yang memiliki komposisi unsur yang proporsinya tidak hanya bilangan bulat.
- Larutan padat = campuran homogen berwujud padat yang terdiri dari satu atau lebih zat terlarut dalam pelarut.

DEFINITION

An ideal crystal can be described in terms a three-dimensionally periodic arrangement of points called lattice and an atom or group of atoms associated with each lattice point called motif:

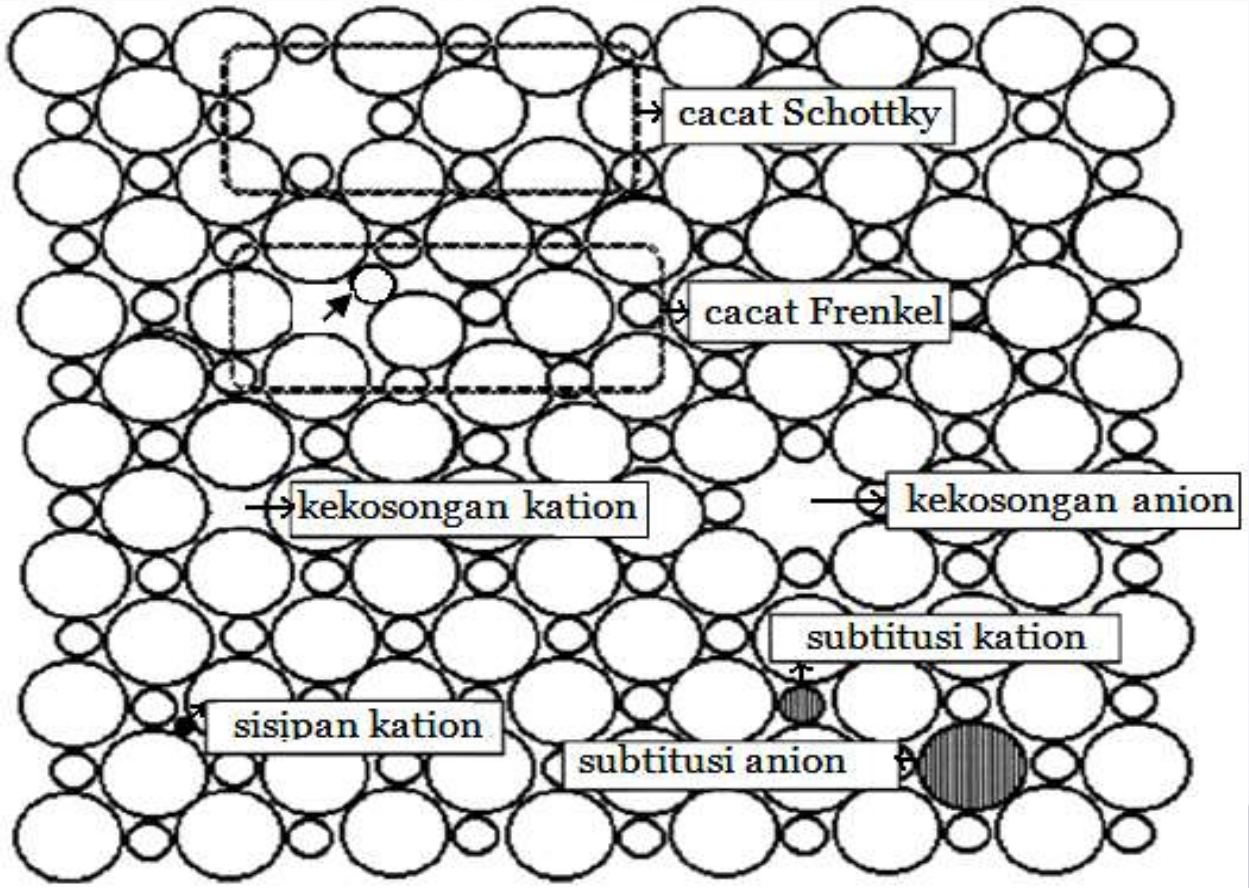
Crystal = Lattice + Motif

However, there can be deviations from this ideality.

These deviations are known as **CRYSTAL DEFECTS**.

POINT DEFECTS

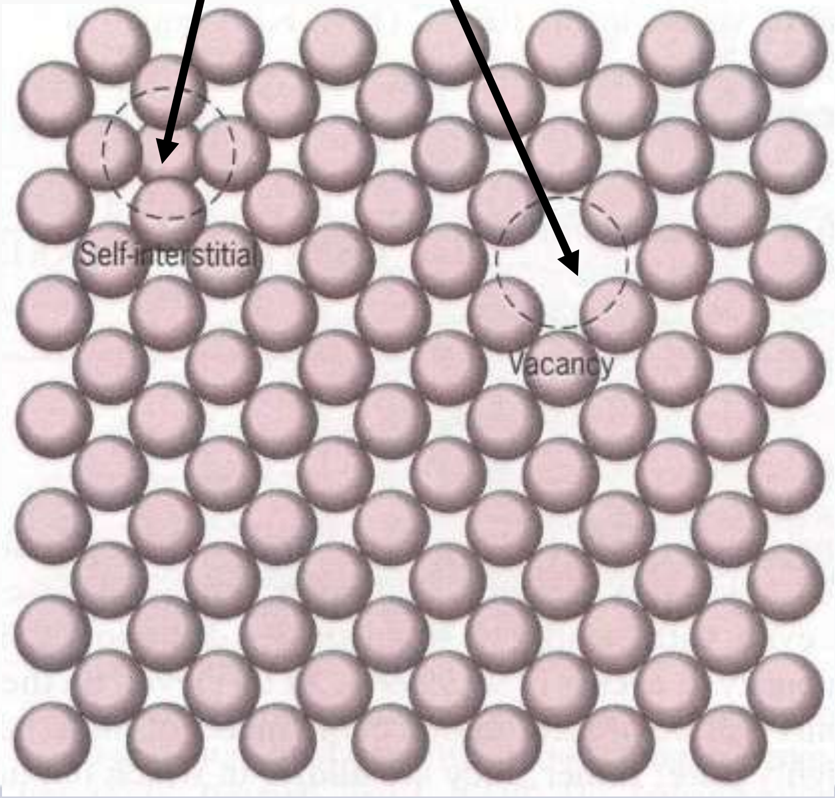
- Intrinsik defects : Occur in pure substances: Schottky defects and Frenkel defects
- Extrinsik defects Due to impurities: Substitutional solid solutions and Interstitial solid solutions

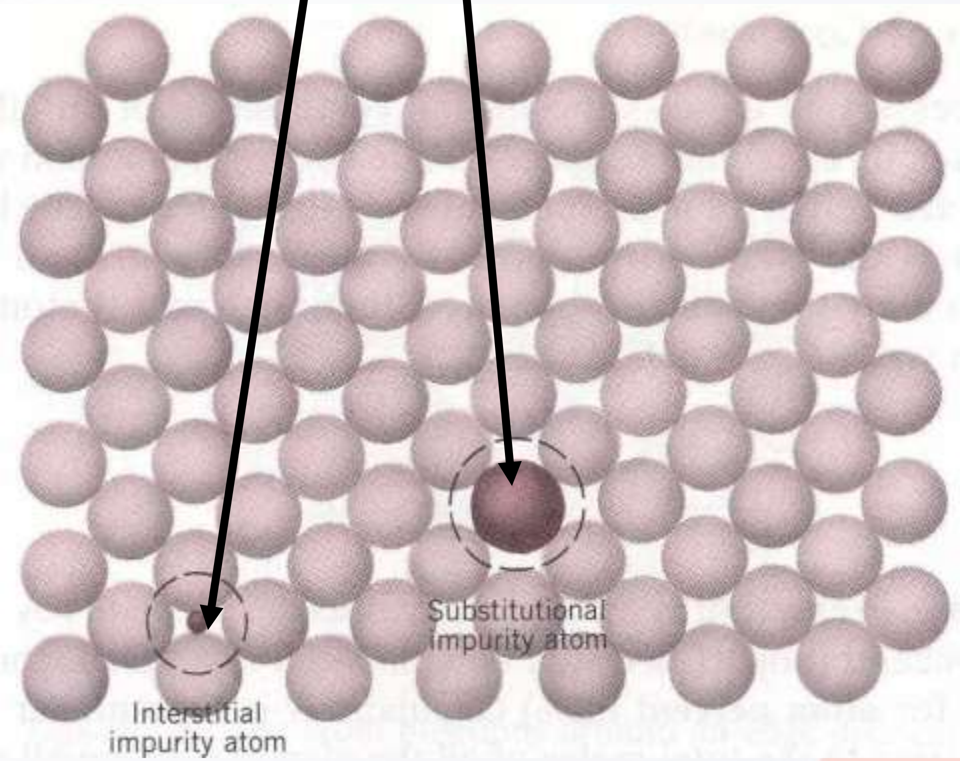


Point Defects

- ***Intrinsic*** defects
  - ***Vacancy***
  - ***Self-interstitial***

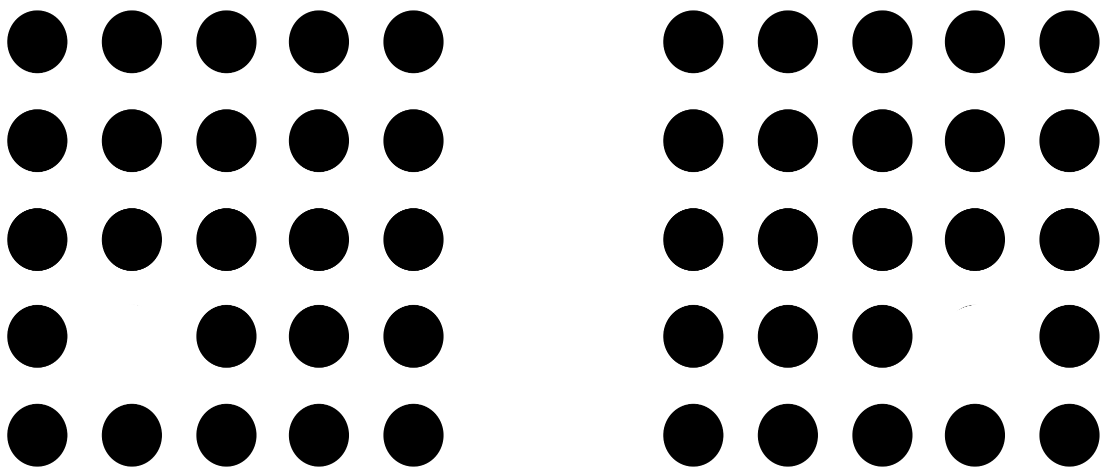
- ***Extrinsic*** defects
  - ***Substitutional impurity***
  - ***Interstitial impurity***





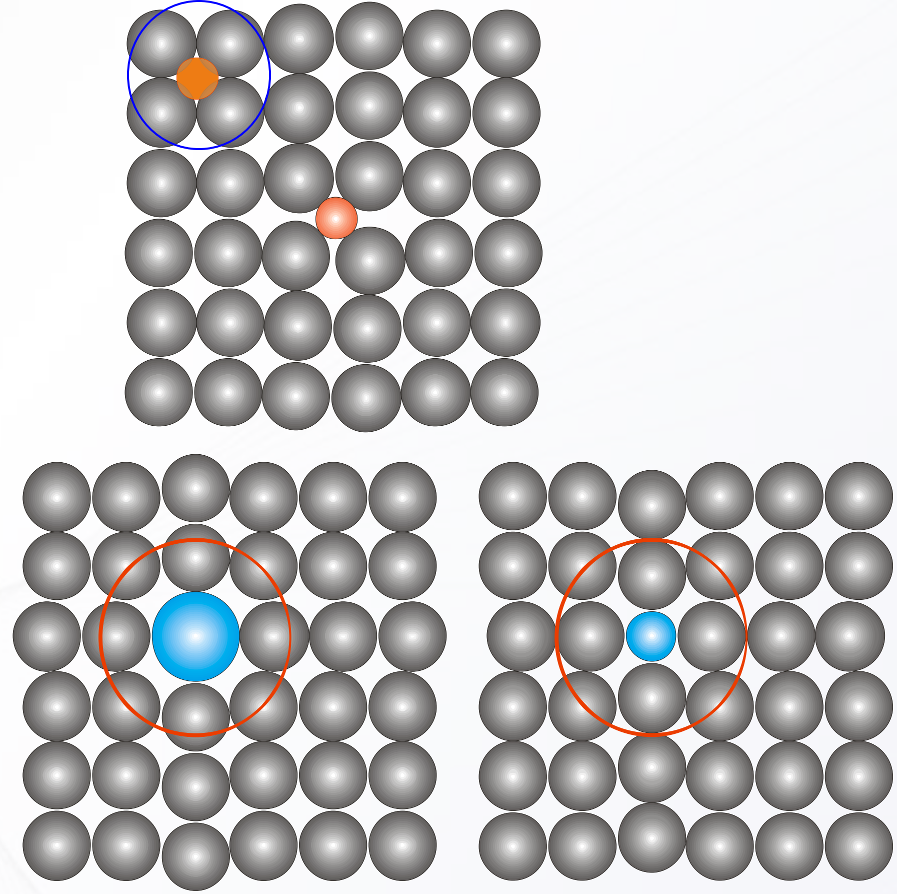
Vacancy

- Missing atom from an atomic site
- Atoms around the vacancy displaced
- Tensile stress field produced in the vicinity



Impurity → Interstitial

Impurity → Substitutional



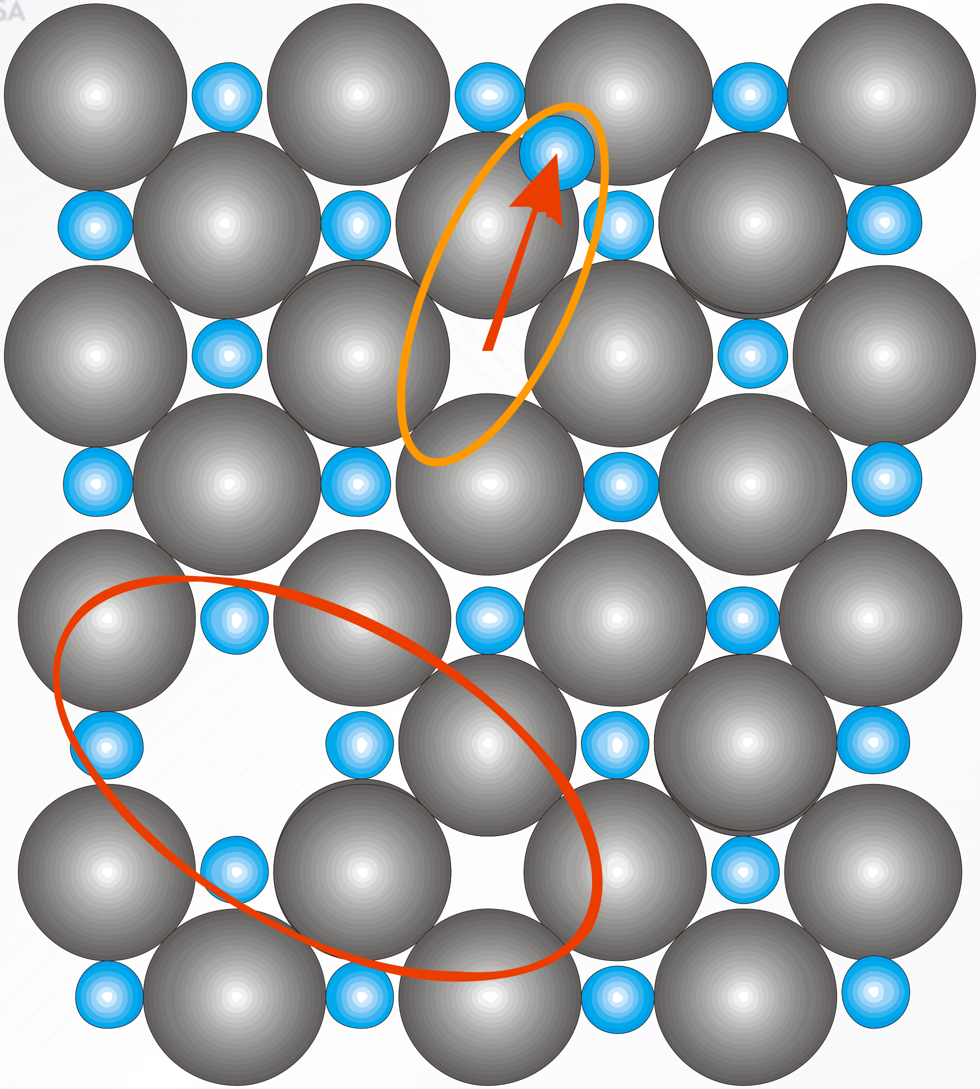
❑ SUBSTITUTIONAL IMPURITY

- Foreign atom replacing the parent atom in the crystal
- E.g. **Cu** sitting in the lattice site of FCC-**Ni**

❑ INTERSTITIAL IMPURITY

- Foreign atom sitting in the void of a crystal
- E.g. **C** sitting in the octahedral void in HT FCC-**Fe**

Defects in ionic solids



Frenkel defect

Cation vacancy
+
cation interstitial

Schottky defect

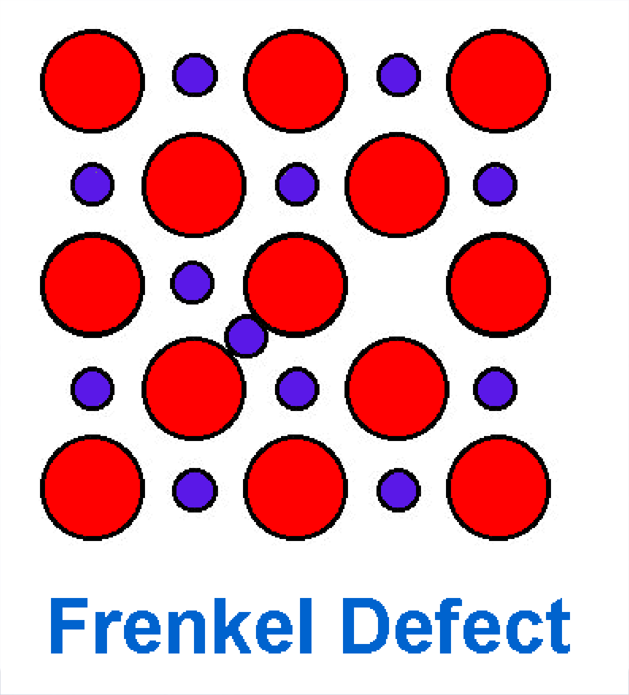
Cation vacancy
+
anion vacancy

Intrinsik Defects -Frenkel

Often a vacancy and interstitial occur together - an ion is displaces from its site into an interstitial position.

This is a **Frenkel Defect** (common in e.g. AgCl) and charge balance is maintained.

Frenkel defects can be induced by irradiation of a sample



Extrinsic defects (due to impurities)

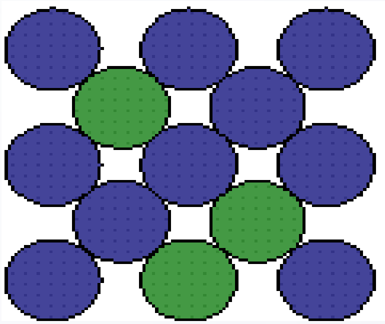
Impurities **or** ***dopants*** **in a solid are any atom(s) of a type that do not belong in the perfect crystal structure (see 'extrinsic semiconductors')**

The host crystal with impurities is called a *solid solution*

Substitutional solid solutions

Impurity atoms occupy the same sites of the host atoms

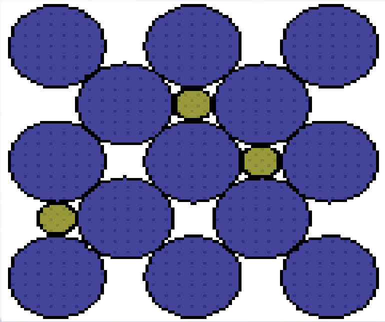
Impurities "substitute" for the host atoms

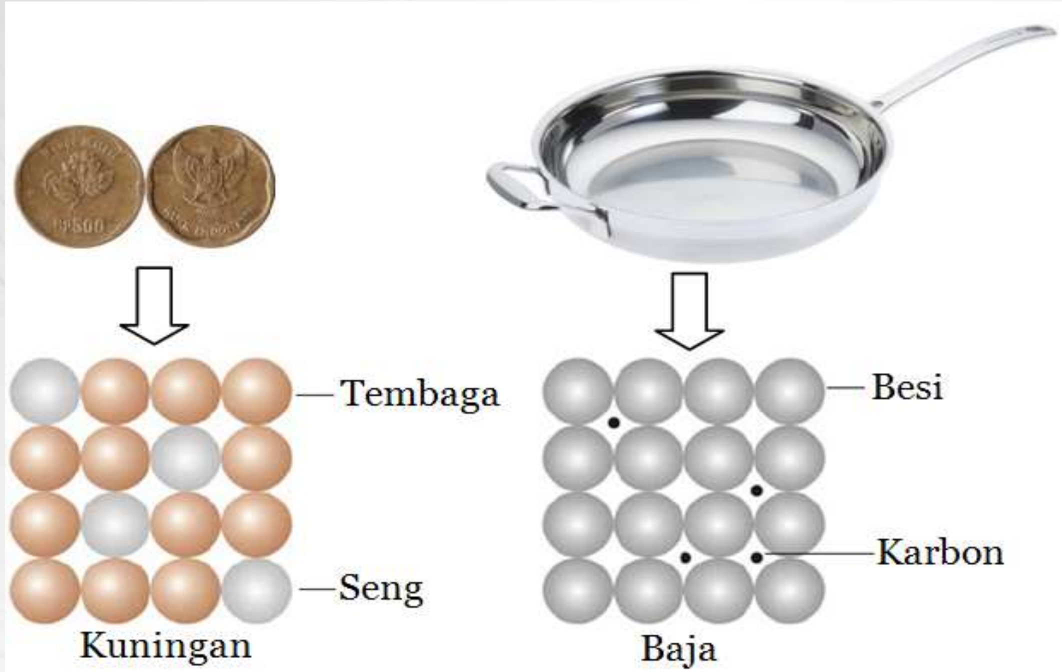


Interstitial solid solutions

Impurity atoms occupy interstices in the host crystal structure

Impurities usually have a small size compared to the host atoms





Gambar. Struktur paduan: kuningan dan baja

- Ada dua jenis paduan (*alloy*) yaitu paduan tersubtitusi dan paduan sisipan.
- Paduan tersubstitusi, contohnya kuningan (sekitar sepertiga dari atom tembaga telah digantikan oleh atom seng).
- Paduan sisipan, Misalnya, baja merupakan paduan dari besi dan karbon.

Impurity defects

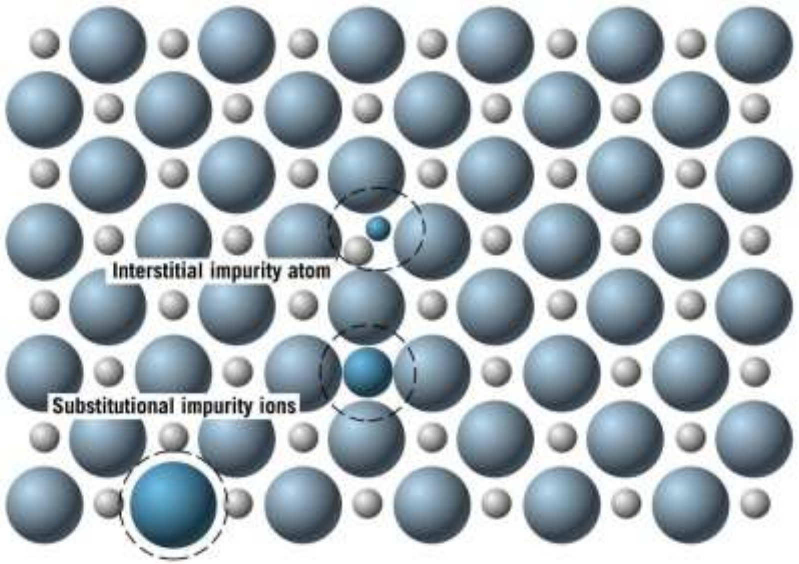


FIGURE 12.23 Schematic representations of interstitial, anion-substitutional, and cation-substitutional impurity atoms in an ionic compound. (Adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. 1, *Structure*, p. 78. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

Charge neutrality must be maintained.

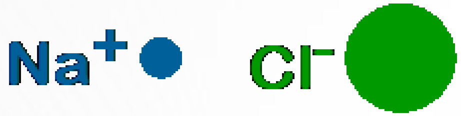
Thus, if a substitutional impurity has a different charge than the substituted ion, another defect (or defects) must be present to balance it out.

Non-stoichiometry often results.

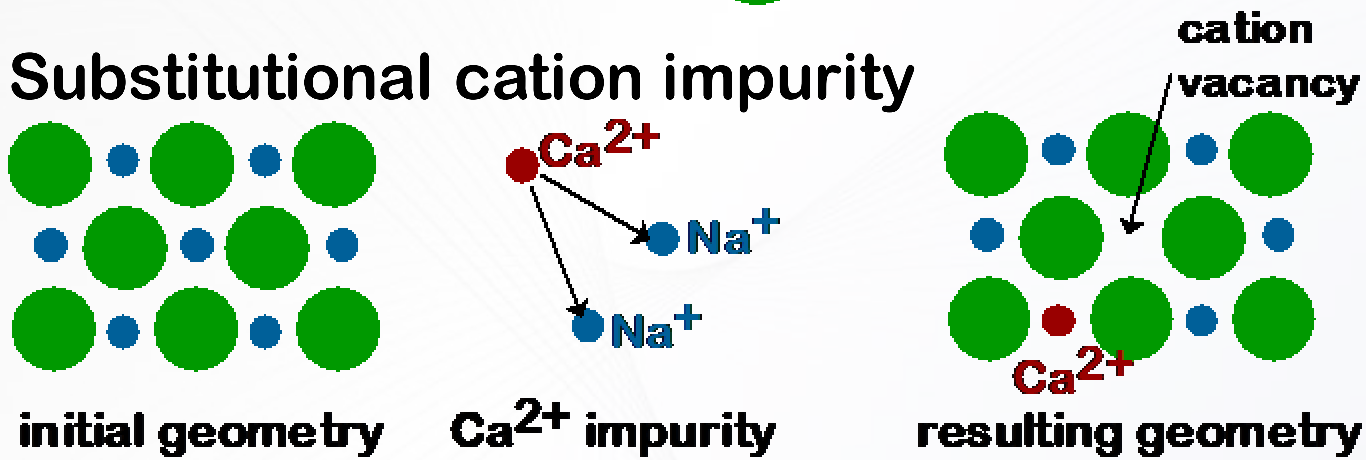
Cationic	**Anionic**
Ca instead of Na in NaCl	O instead of Cl in NaCl
B instead of Si in SiO_2	O instead of N in GaN

IMPURITIES

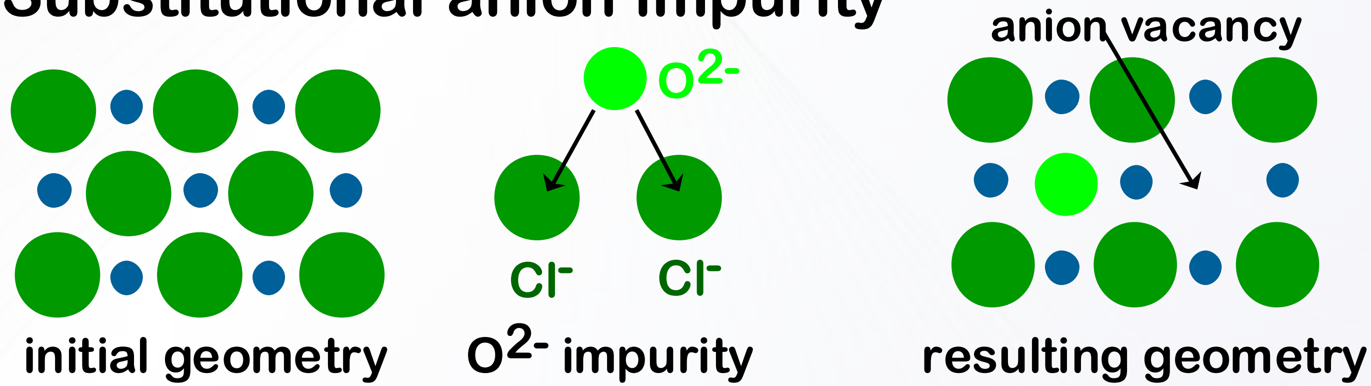
- Impurities must satisfy **charge balance**
- Ex: NaCl



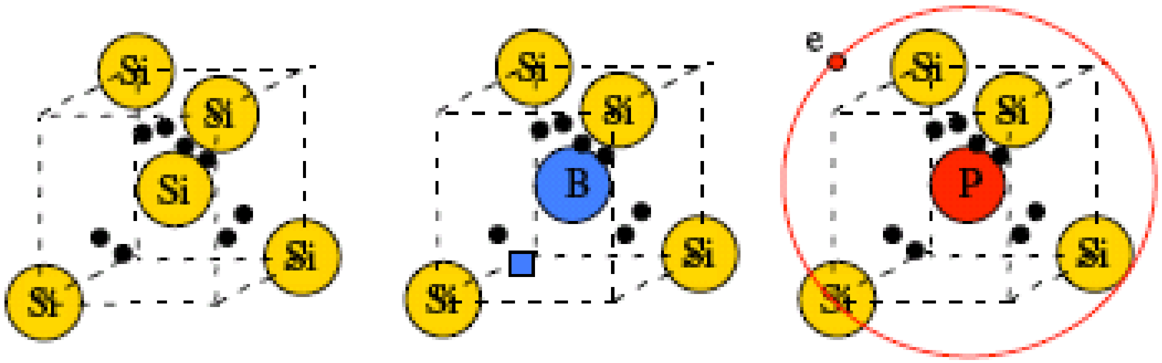
- Substitutional cation impurity



- Substitutional anion impurity

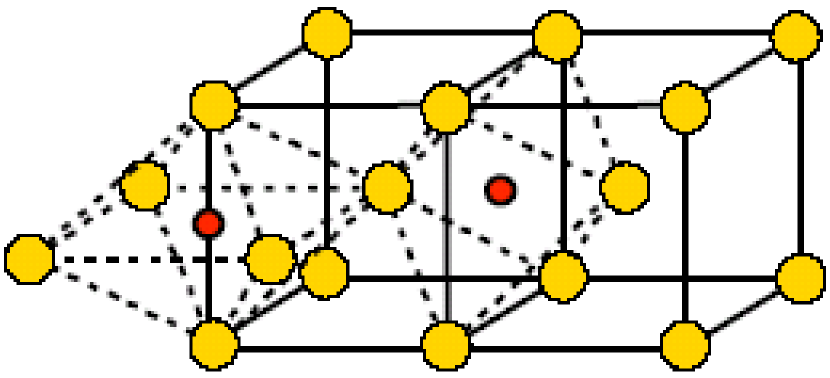


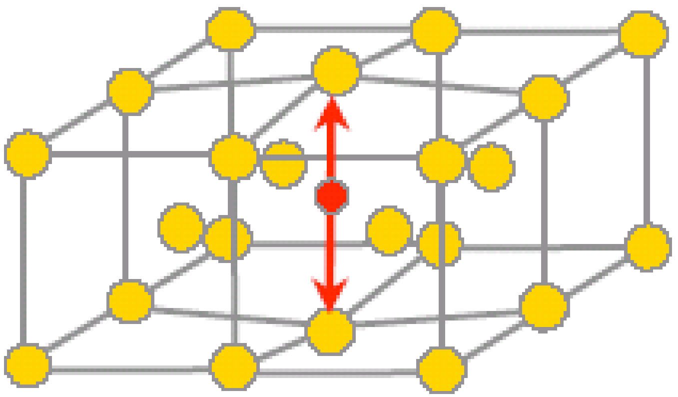
Substitutional Solutes: Electrical Defects in Semiconductors



- Solutes can control the number and type of carriers in Si
- P (z = 5) introduces an electron in an excited state
  - Electron can be liberated to conduct electricity
  - "Donor" solutes create "n-type" extrinsic semiconductors
- B (z = 3) leaves a hole in a bonding state
  - Hole can "accept" an electron to create a mobile positive charge
  - "Acceptor" solutes create "p-type" extrinsic semiconductors

Interstitial Solutes: Carbon in Steel



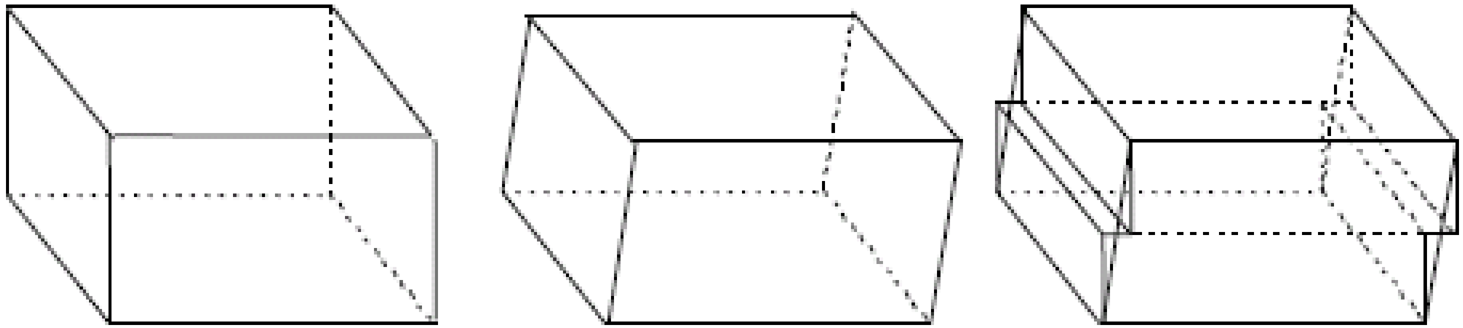


- Carbon interstitials fill octahedral sites in bcc Fe
  - Octahedral has larger volume (smaller radius) than tetrahedral
- Octahedral sites are asymmetric
  - Sites distort, creating local strain
  - Makes deformation difficult, strengthens material

LINE DEFECTS
(DISLOCATIONS)

- Plastic deformations by Slip
- Edge Dislocations
- Screw Dislocations
- Mixed Dislocation

Line Defects: Plastic Deformation by Slip



- Plastic deformation is a change in shape
  - Changes in shape happen by shear
  - Equivalent to simple shear shown
- Shear happens by "slip"
  - Planes of atoms slip over one an other like cards in a deck
  - Slip is accomplished by linear defects - "dislocations"

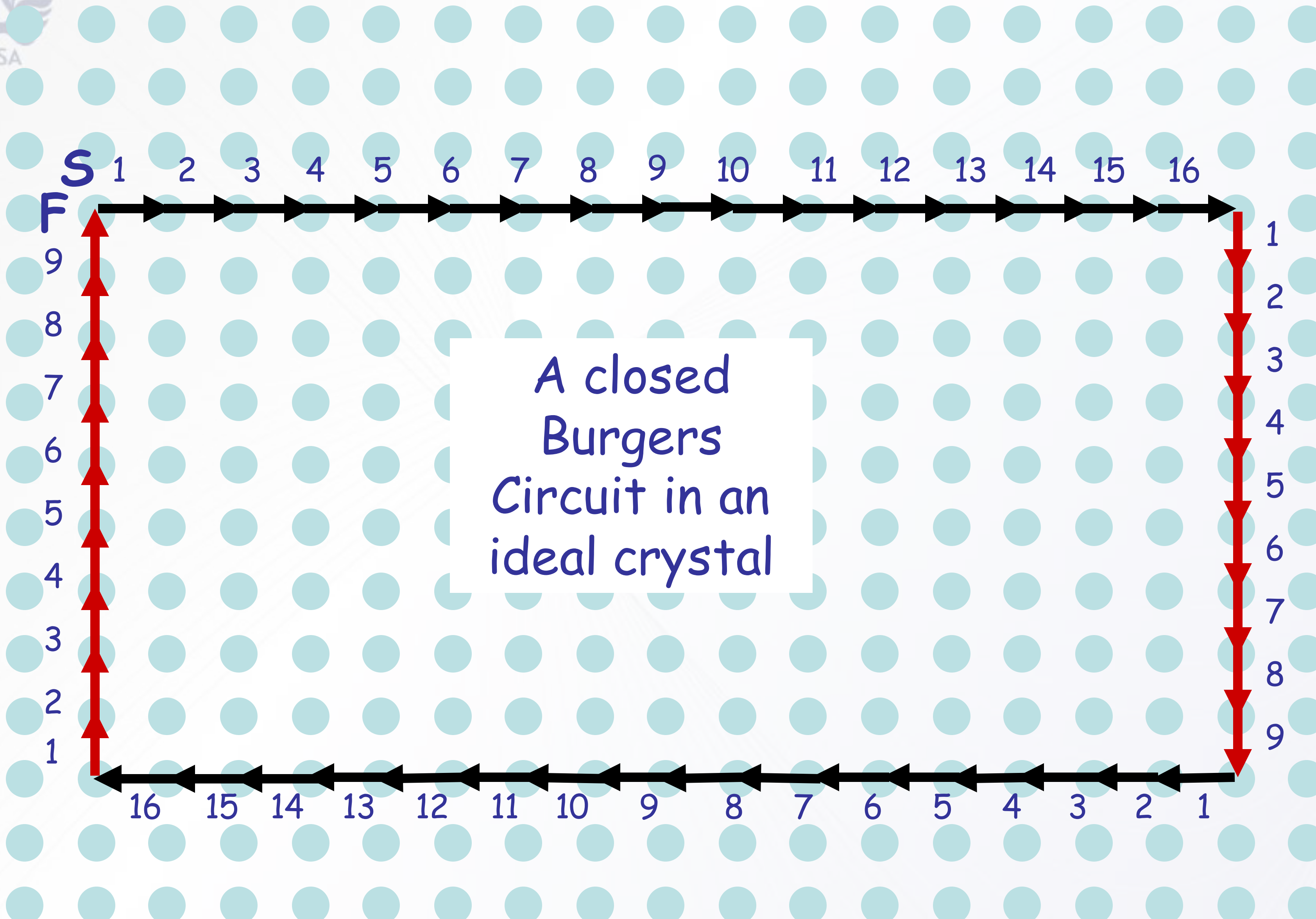
Mechanism of plastic deformation in crystals: <u>dislocation glide</u>, or slip of atomic planes (atomic planes move one by one via the formation and movement of dislocations, rather than all the planes move simultaneously)

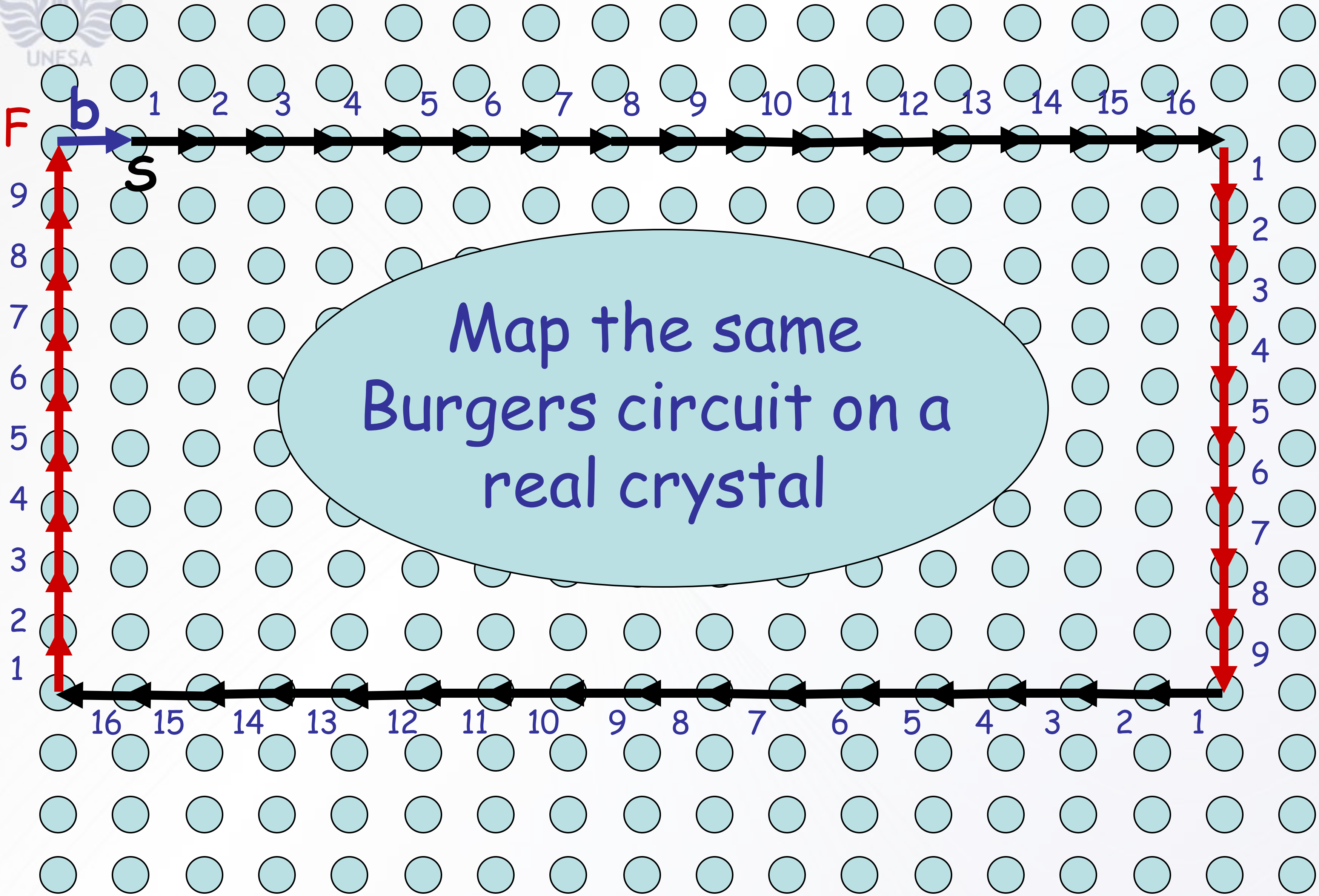
Burgers vector

Johannes Martinus BURGERS

~~Burger's vector~~

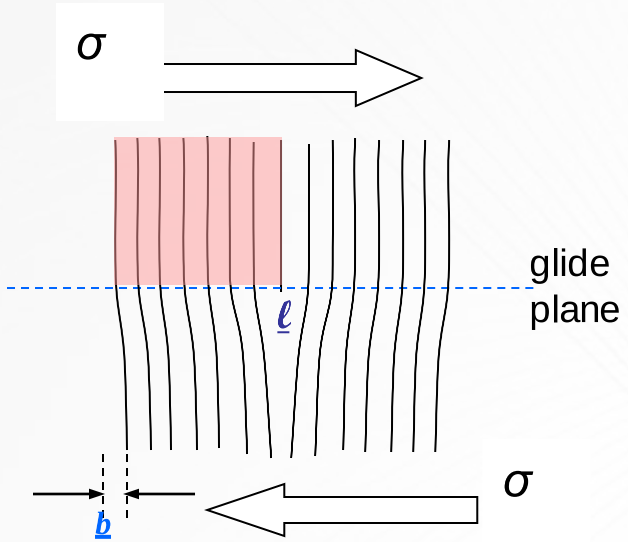
Burgers vector


A closed Burgers Circuit in an ideal crystal
S
F



RHFS convention

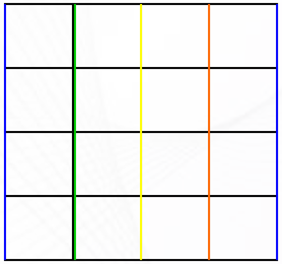
Definitions



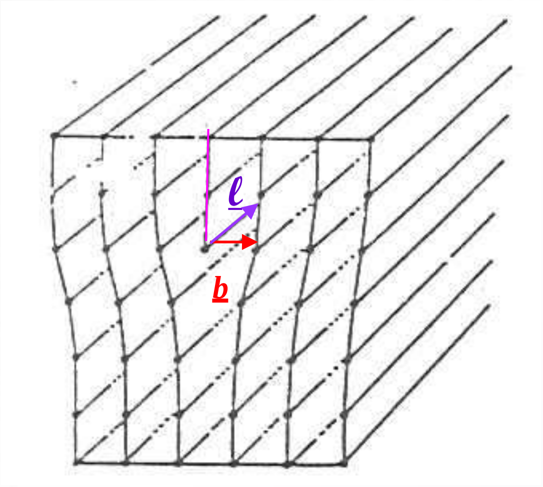
- The boundary plane across which shear occurs is the glide plane
- The boundary line that separates slipped (red) and unslipped regions is the dislocation line or axis ***ℓ***
- The direction and magnitude of slip = Burger's vector, ***b***
- *b* is in general a lattice vector, so there is no long range mismatch between slipped and unslipped planes
- If *b* is parallel to *ℓ* dislocation is 'screw'
- If *b* is perpendicular to *ℓ* dislocation is 'edge'

Edge and Screw Dislocations

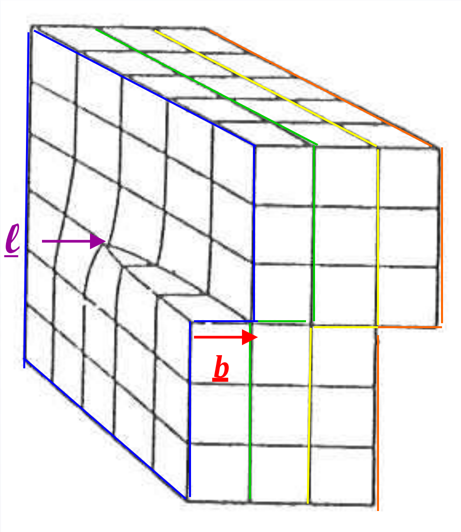
Perfect crystal lattice



Edge dislocation:
"extra plane"



Screw dislocation
(distortion of the
crystal)

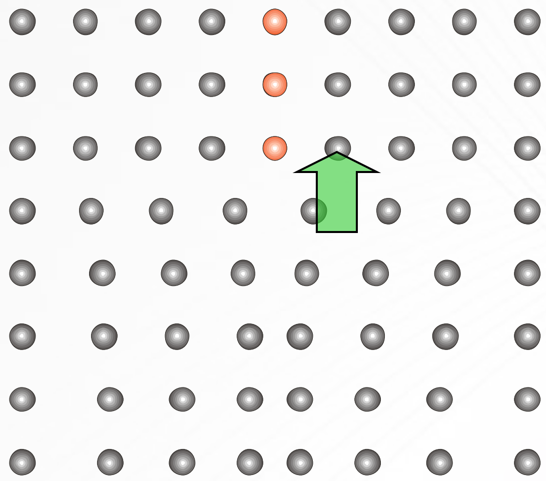


Motion of Edge dislocation

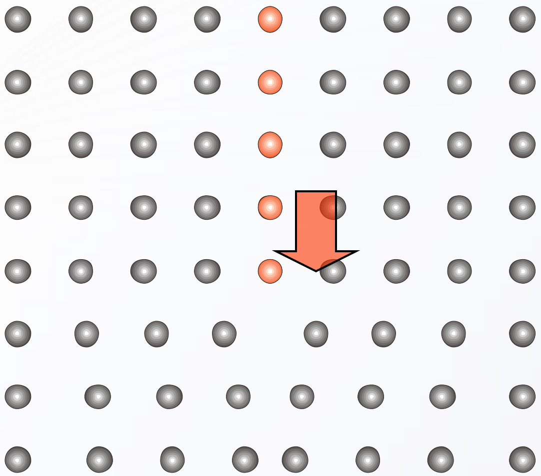
- Conservative *(Glide)* — Motion of dislocations On the slip plane
- Non-conservative *(Climb)* — Motion of dislocation ⊥ to the slip plane

- For edge dislocation: as **b** ⊥ **l**
- Climb involves addition or subtraction of a row of atoms below the half plane
  - ► positive climb = climb up → removal of a plane of atoms
  - ► negative climb = climb down → addition of a plane of atoms

Edge Climb

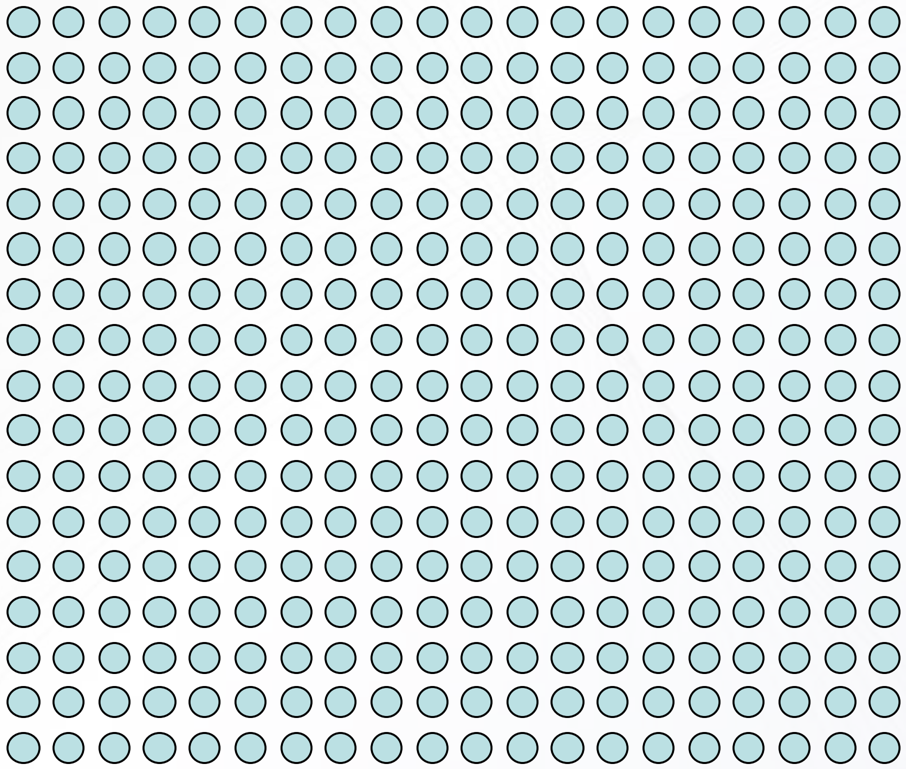


Positive climb
Removal of a row of atoms

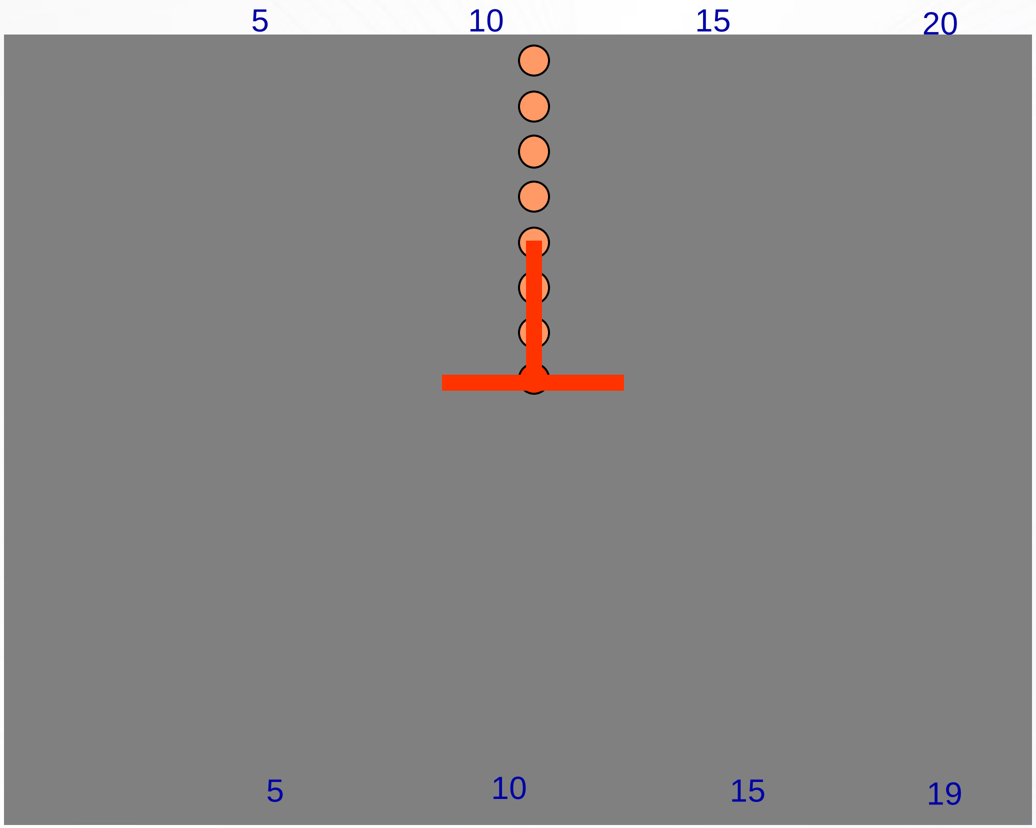


Negative climb
Addition of a row of atoms

Let's look at the atoms in a perfect crystal

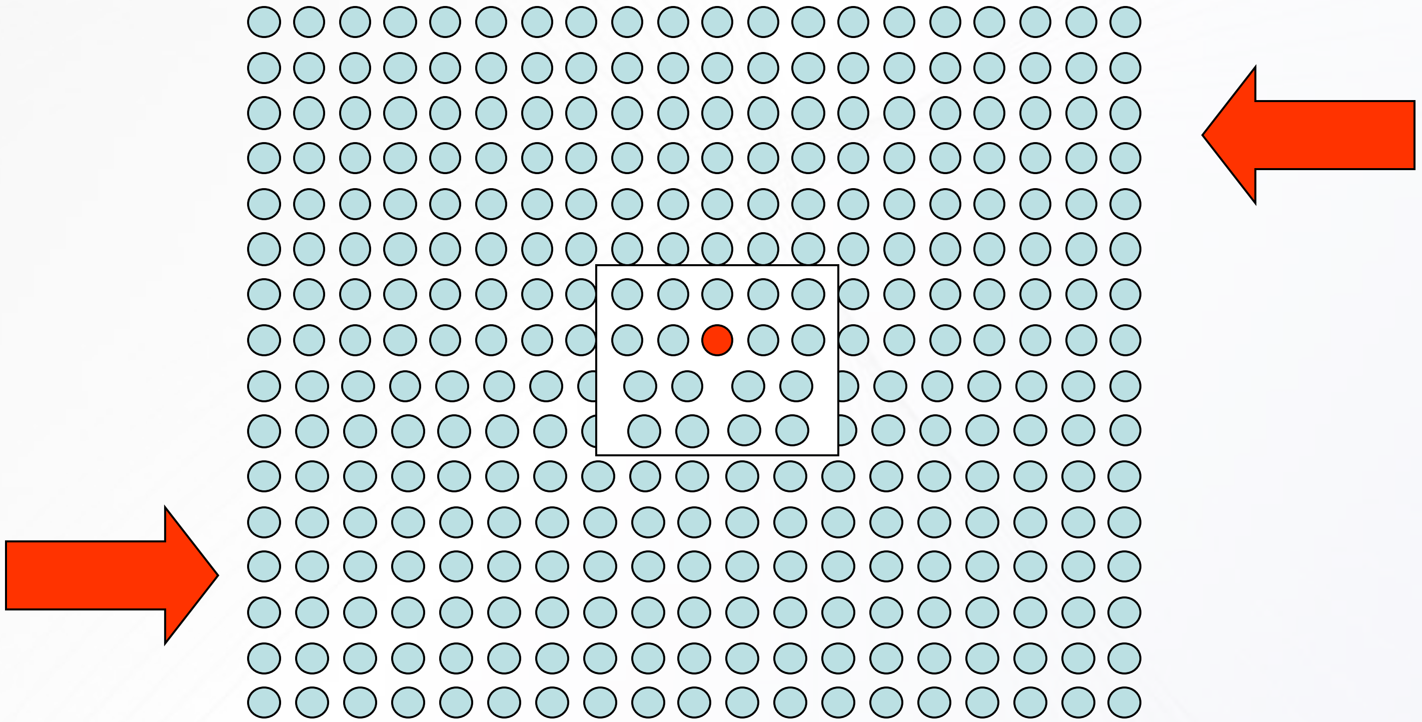


Let's look at the atoms in a <u>realistic</u> crystal

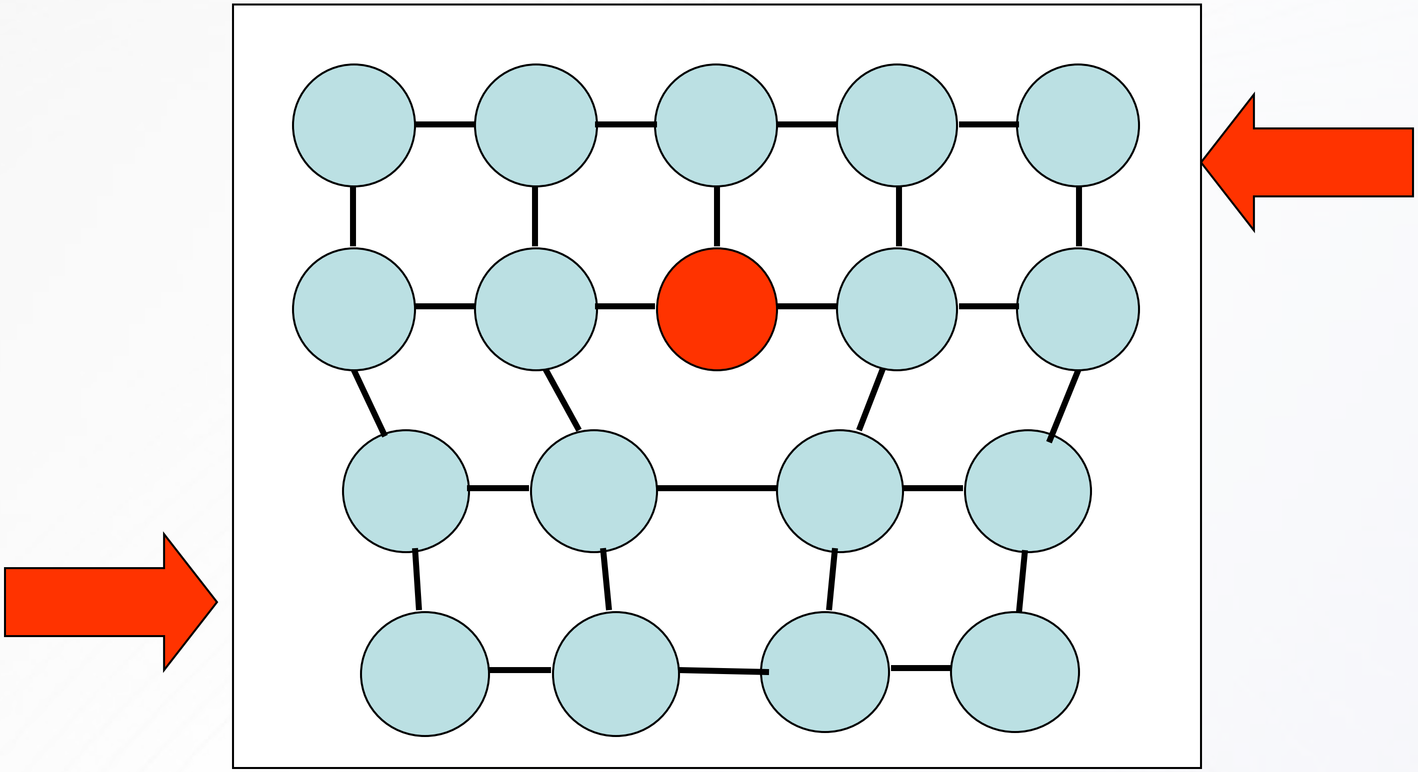


⊥ = **"Edge dislocation"**

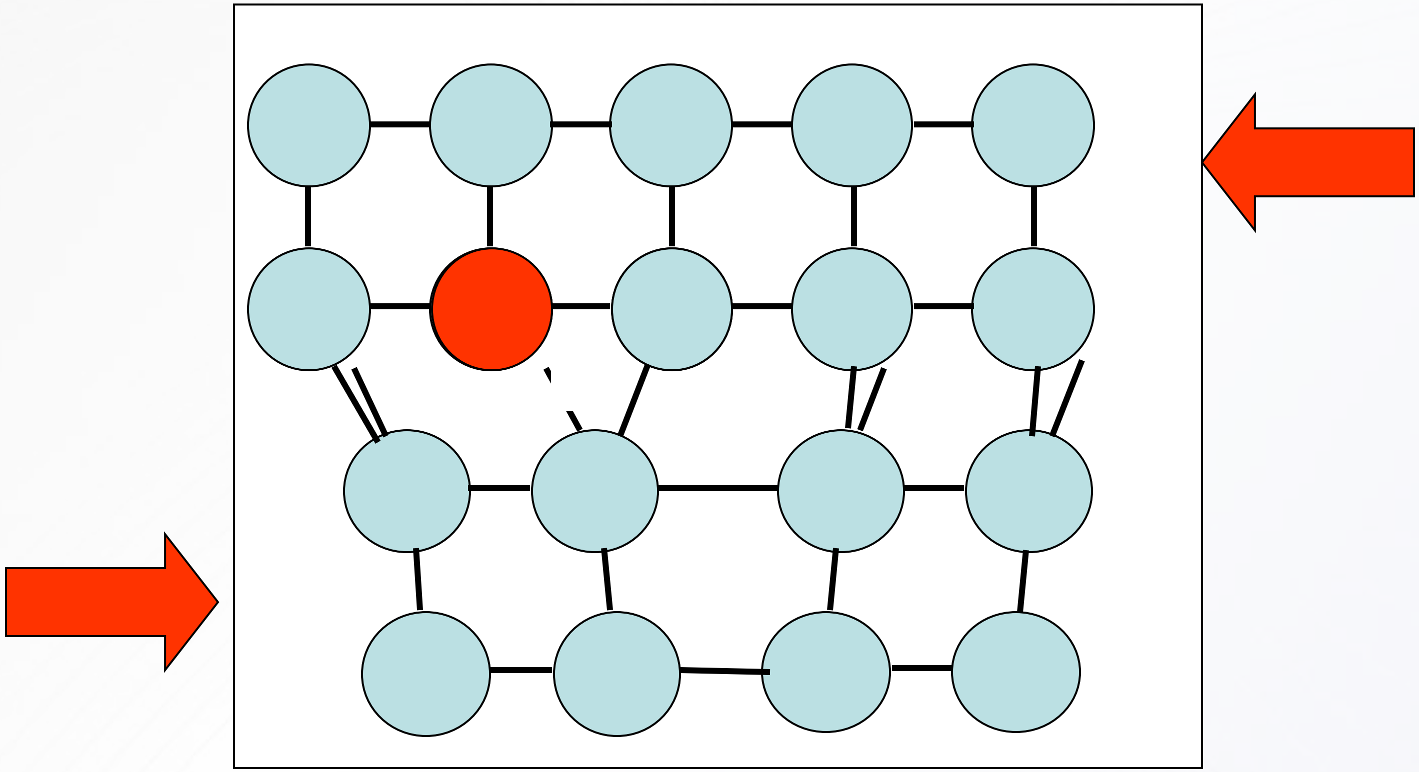
“glide”edge dislocations



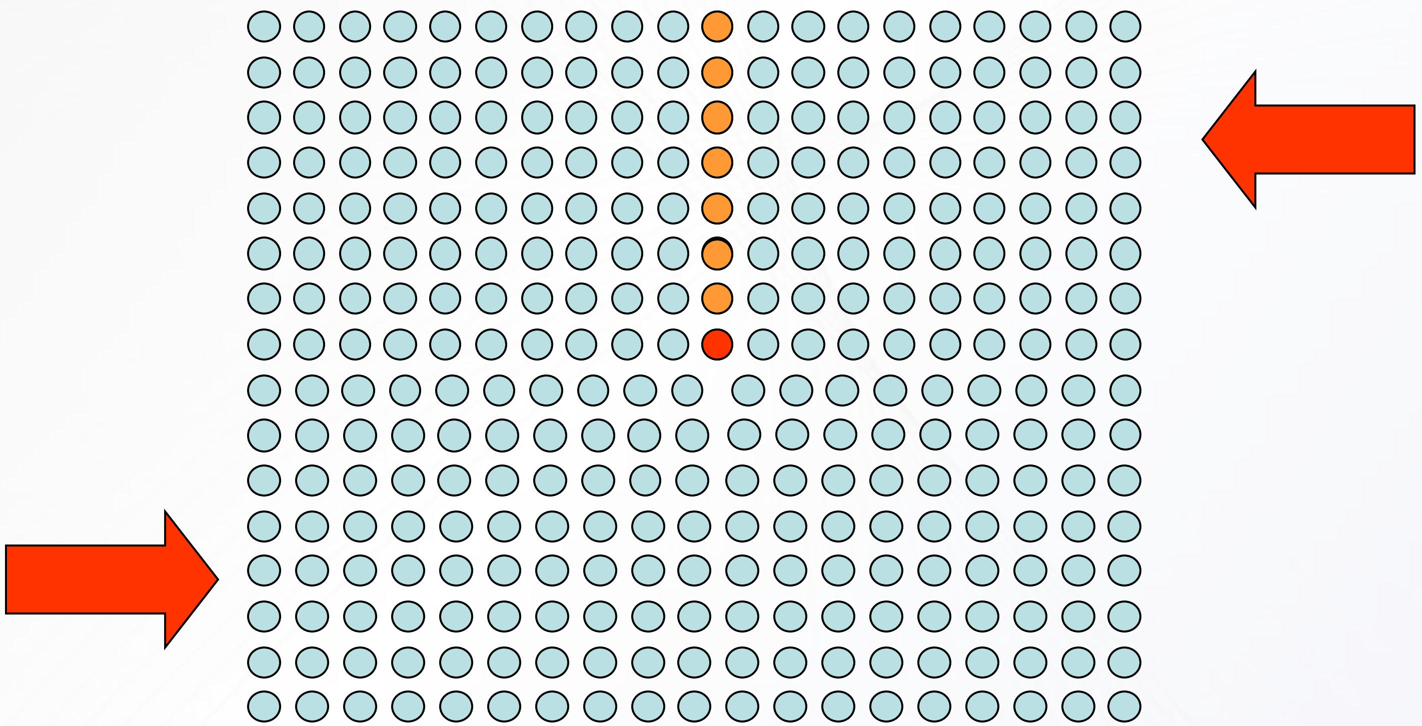
“glide”edge dislocations



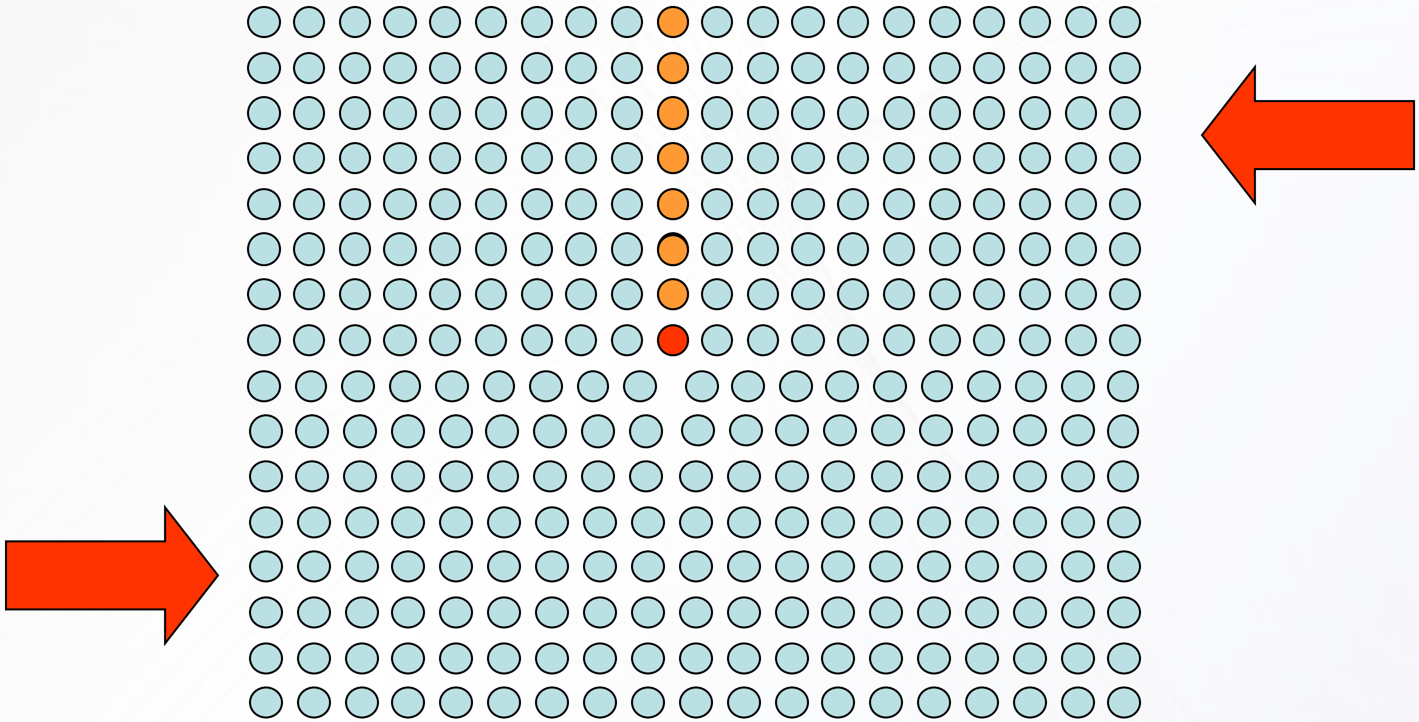
“glide”edge dislocations



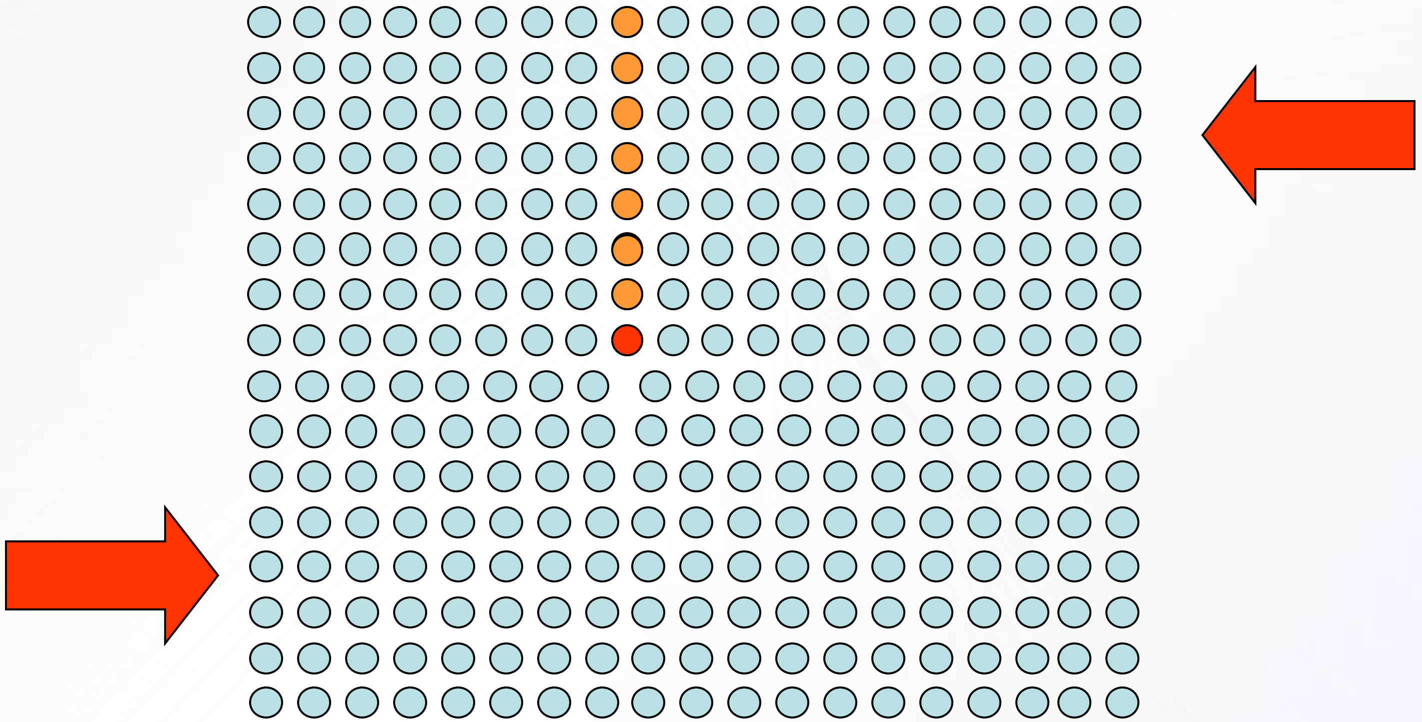
“glide”edge dislocations



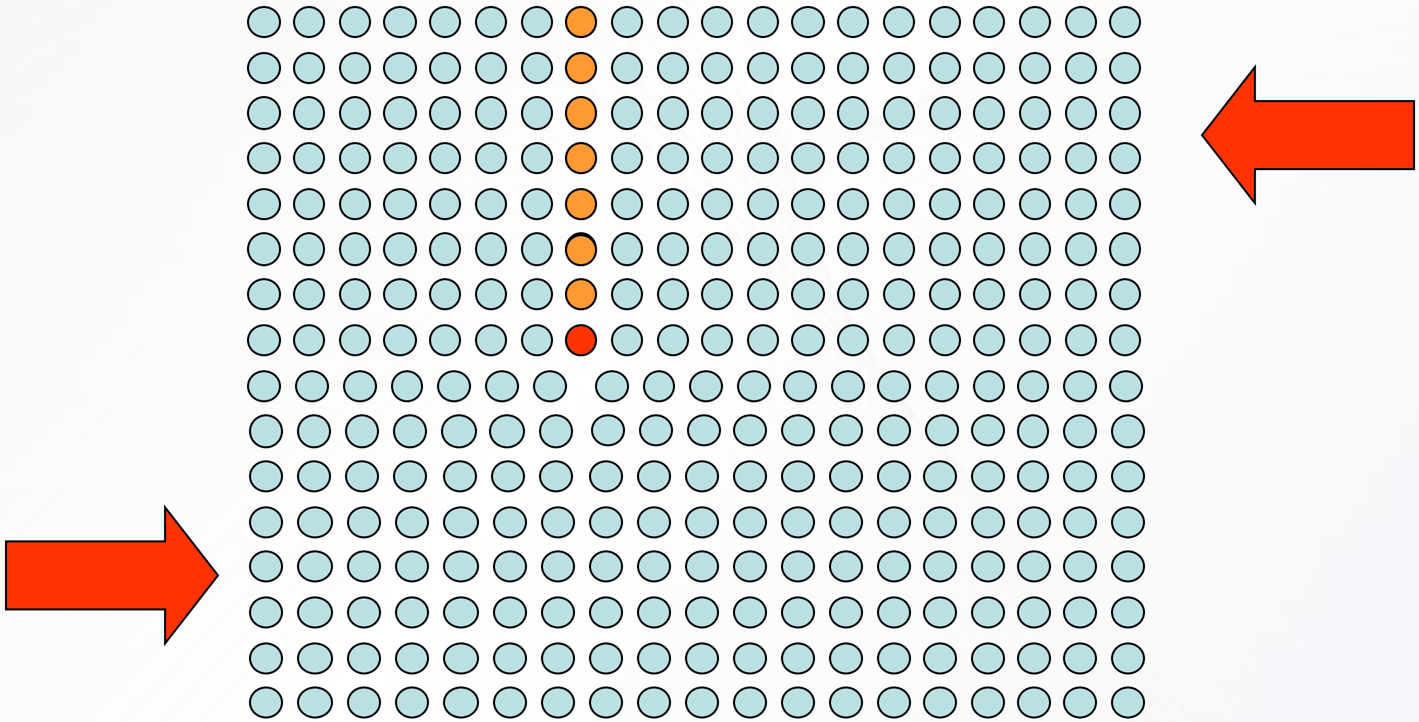
“glide”edge dislocations



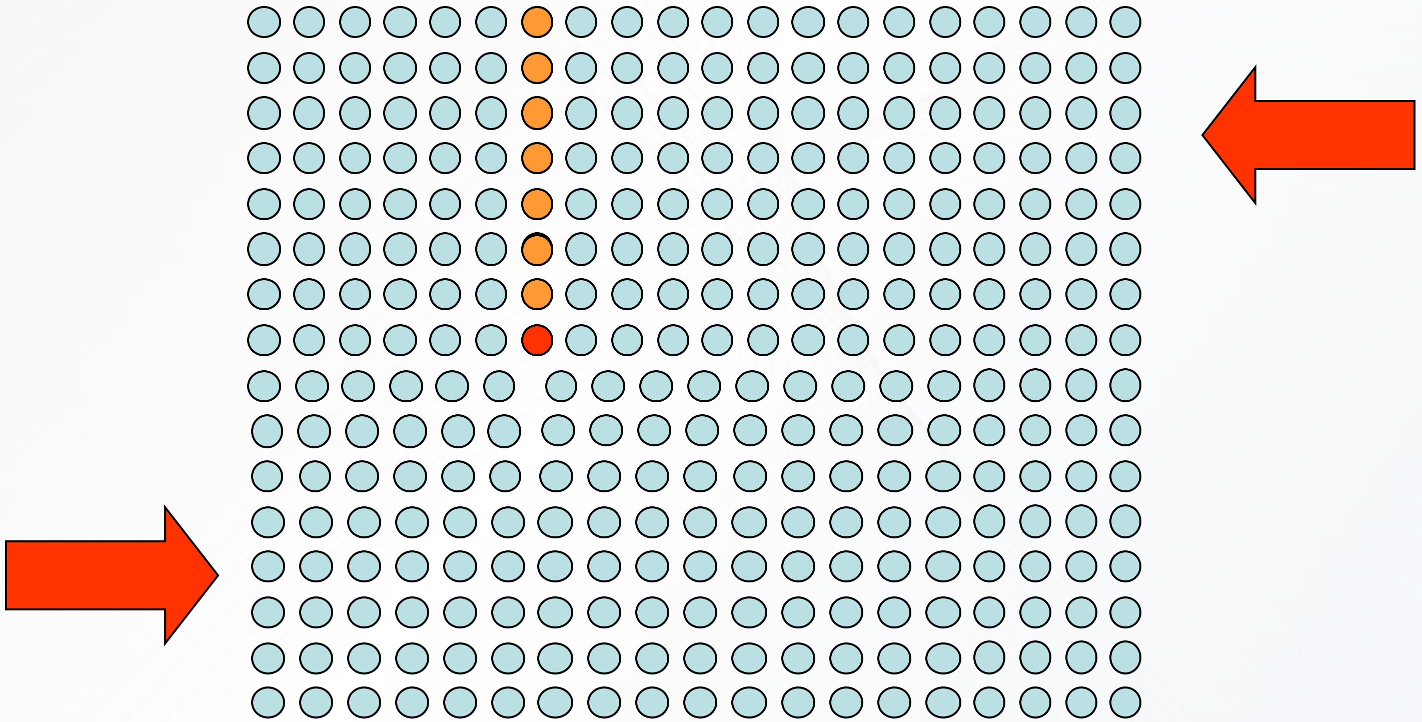
“glide”edge dislocations



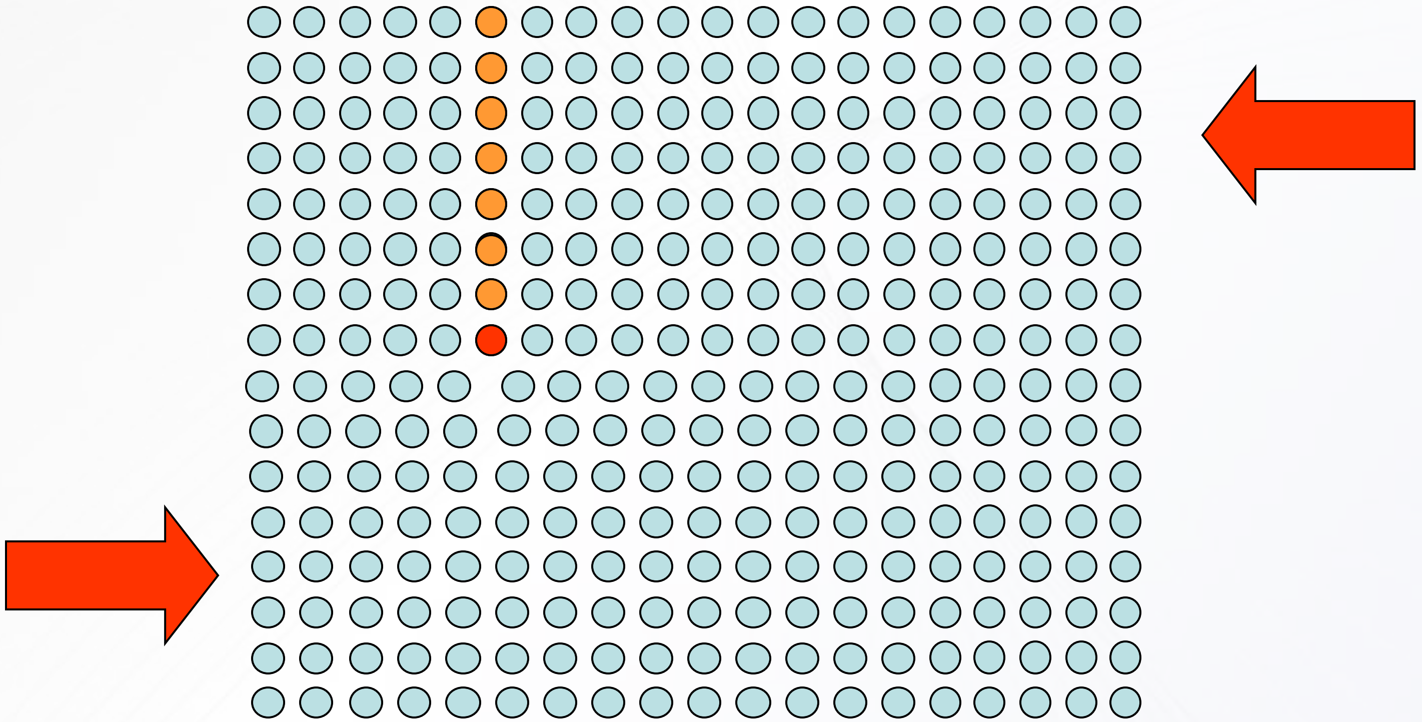
“glide”edge dislocations



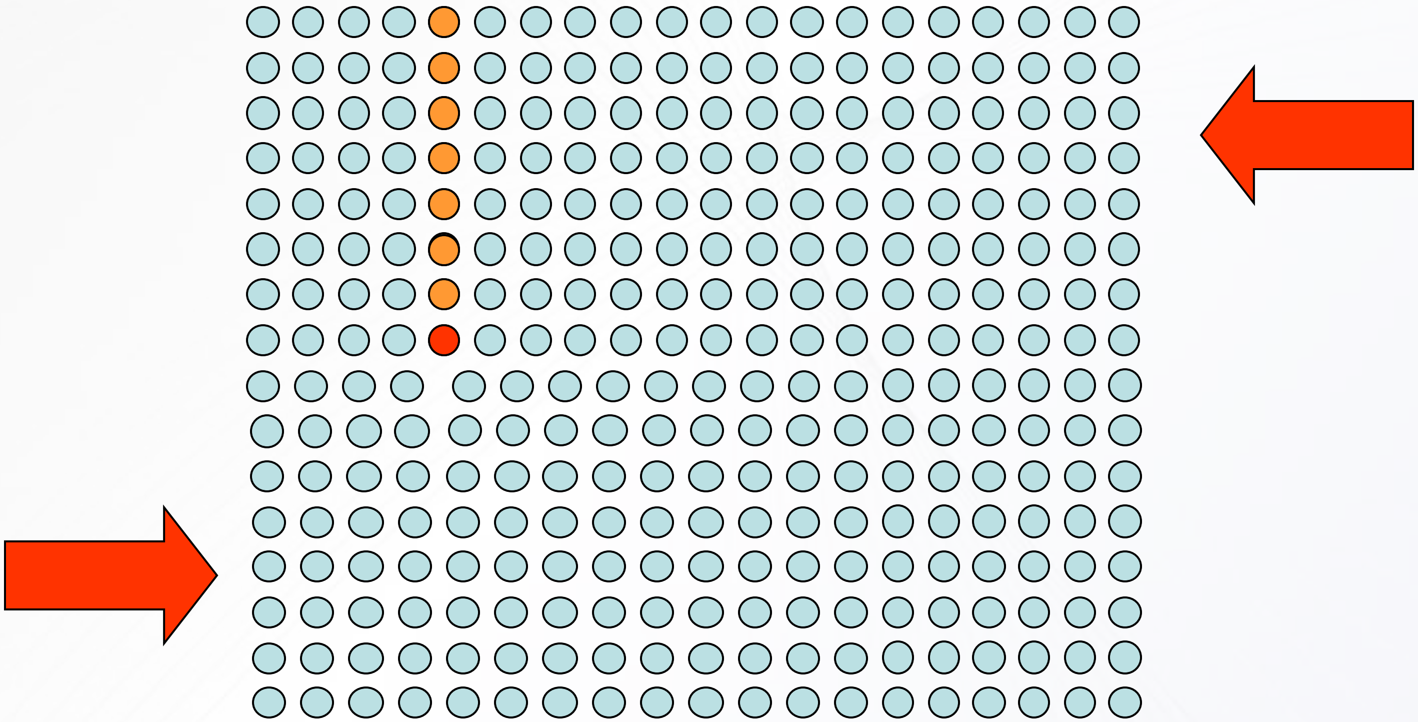
“glide”edge dislocations



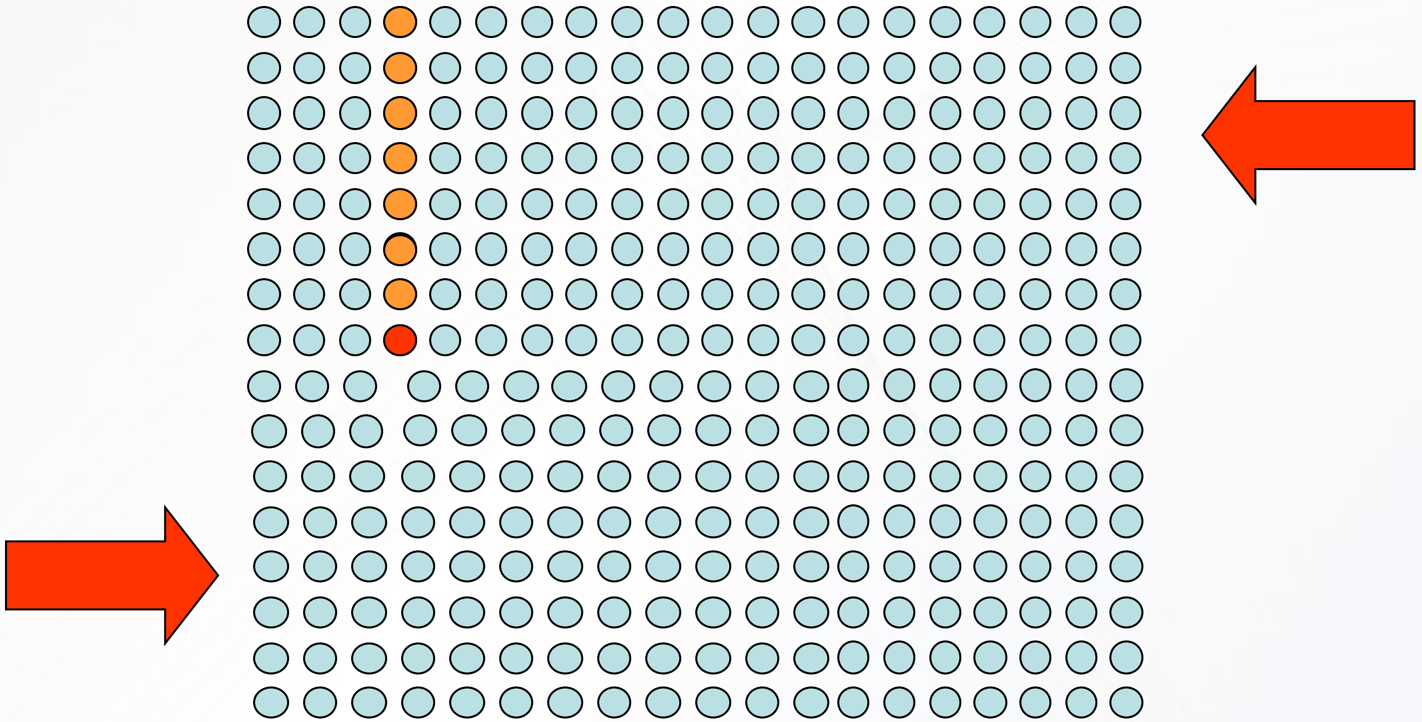
“glide”edge dislocations



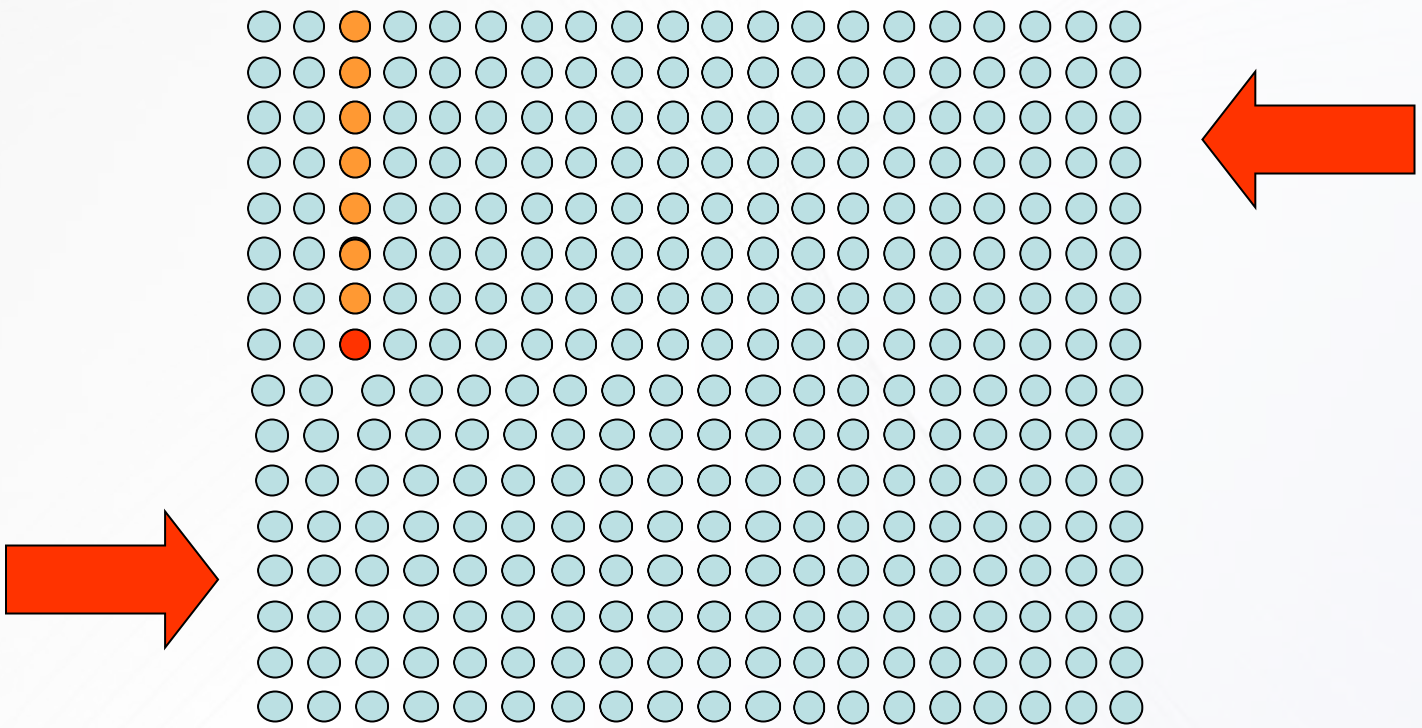
“glide”edge dislocations



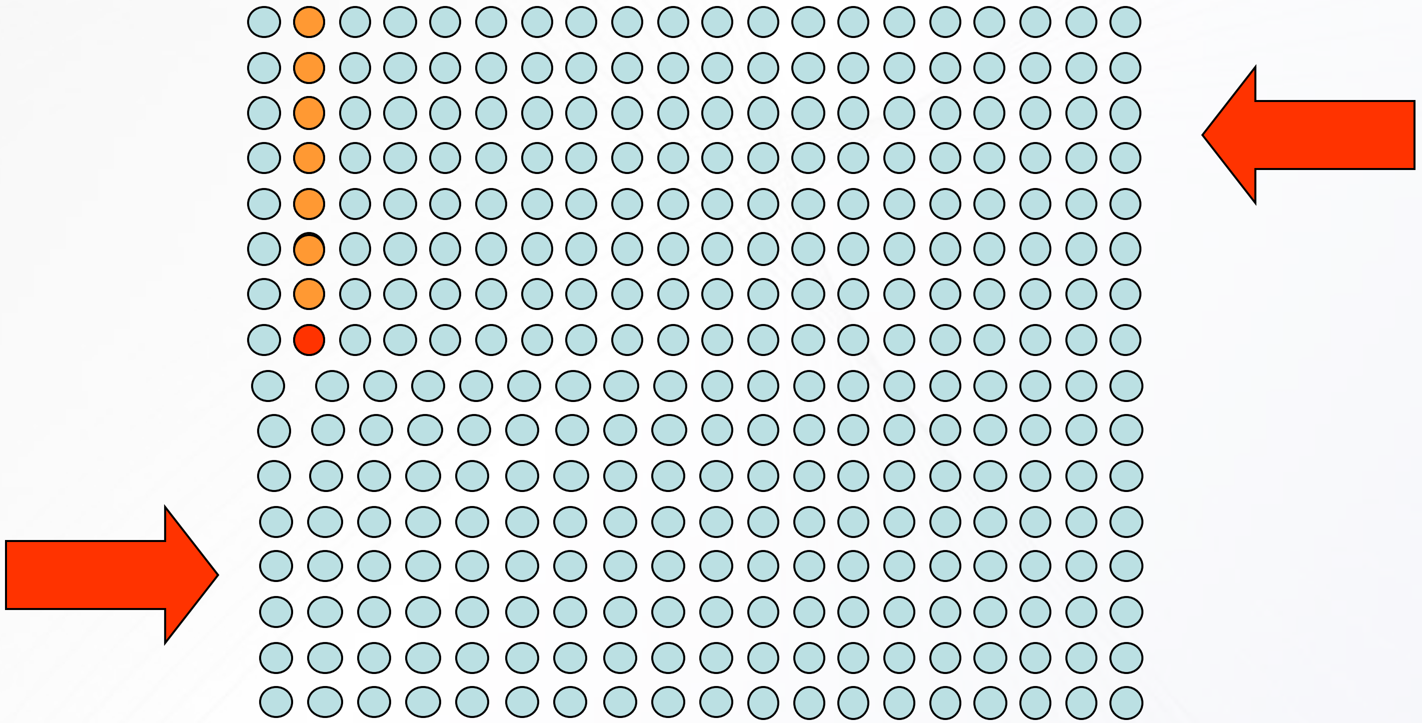
“glide”edge dislocations



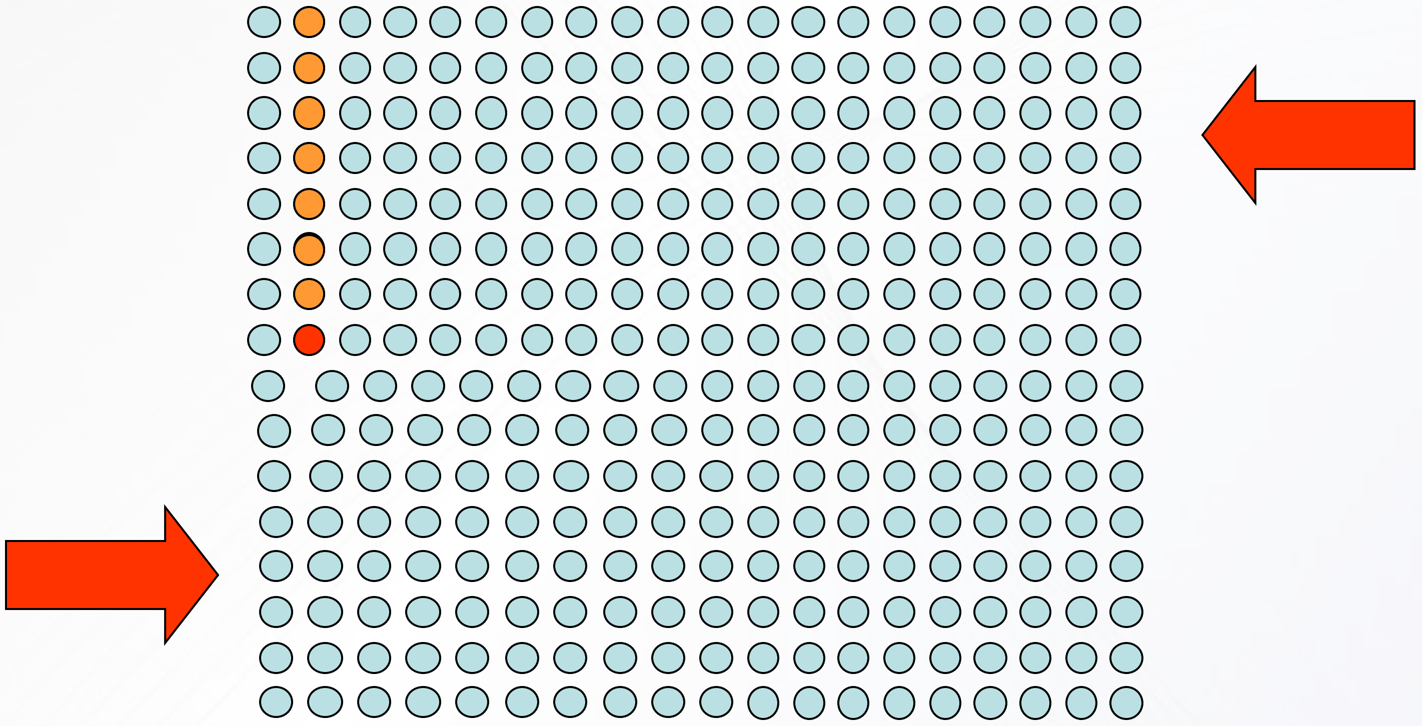
“glide”edge dislocations



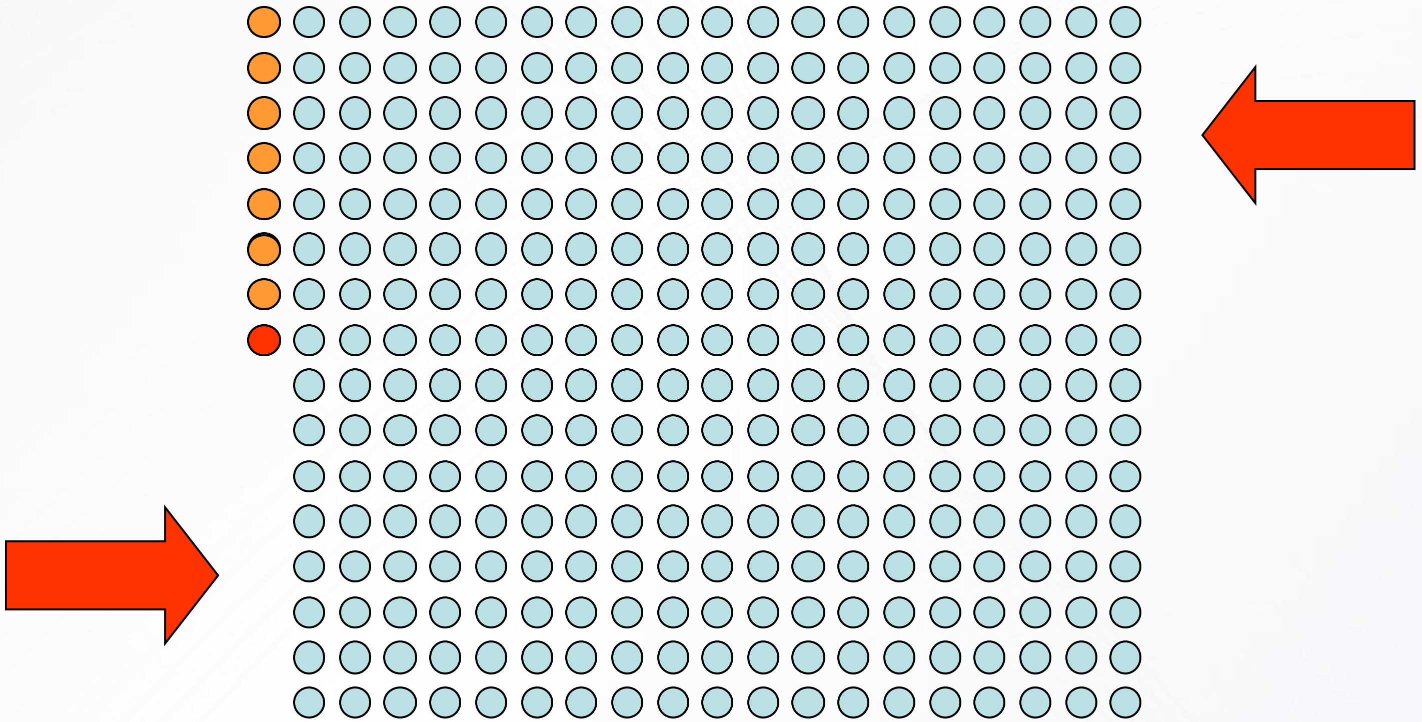
“glide”edge dislocations



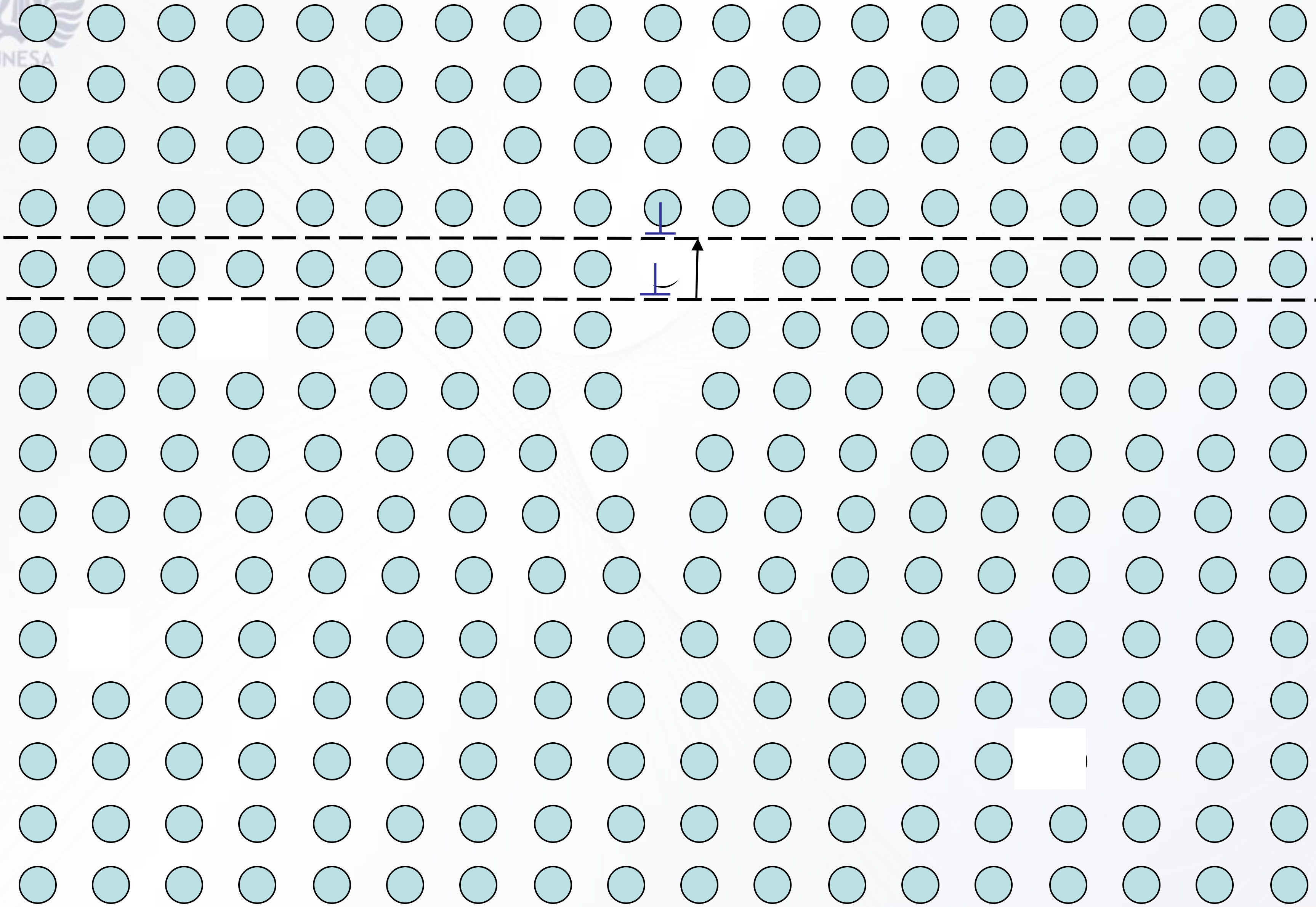
“glide”edge dislocations



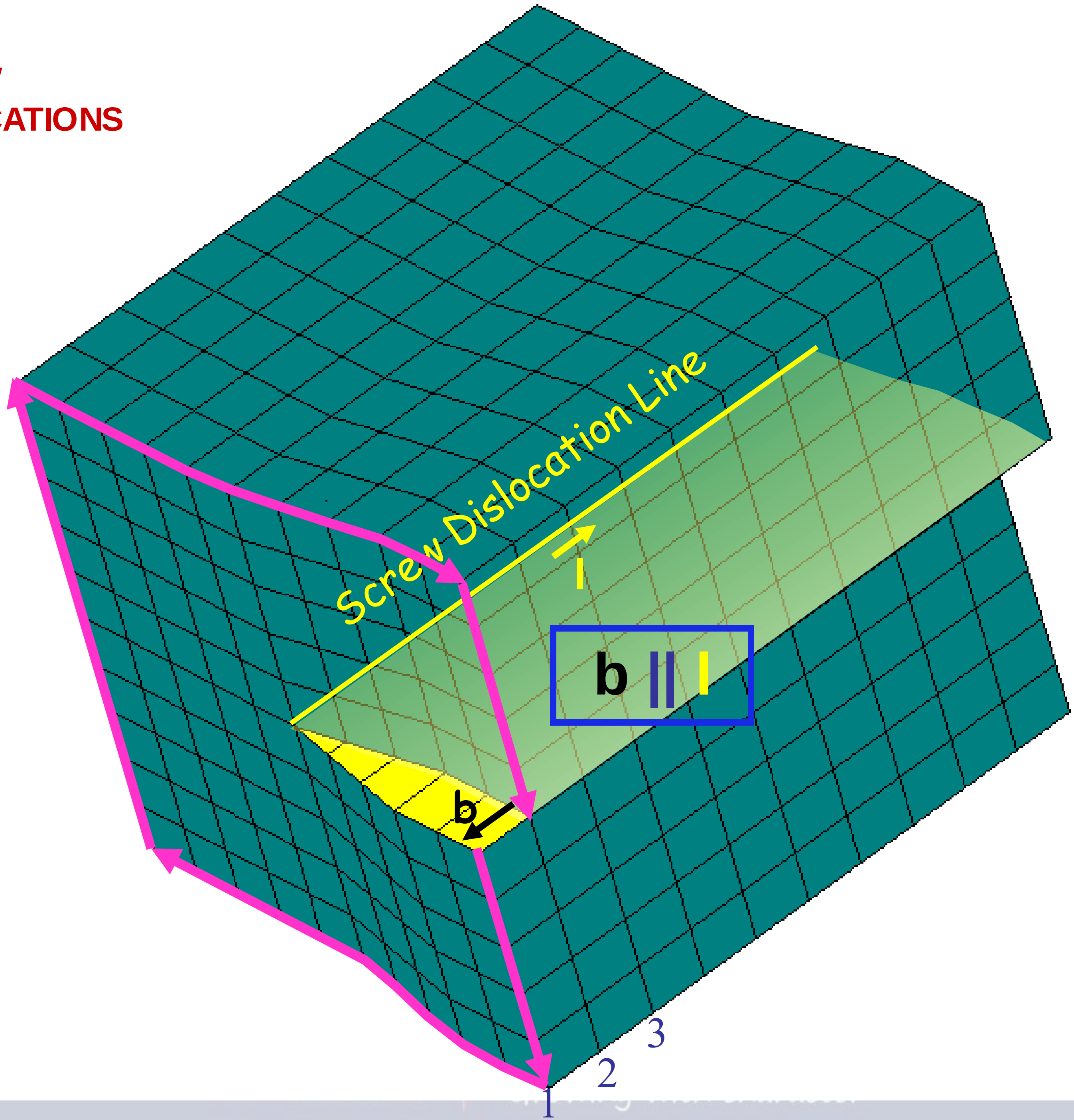
“glide”edge dislocations



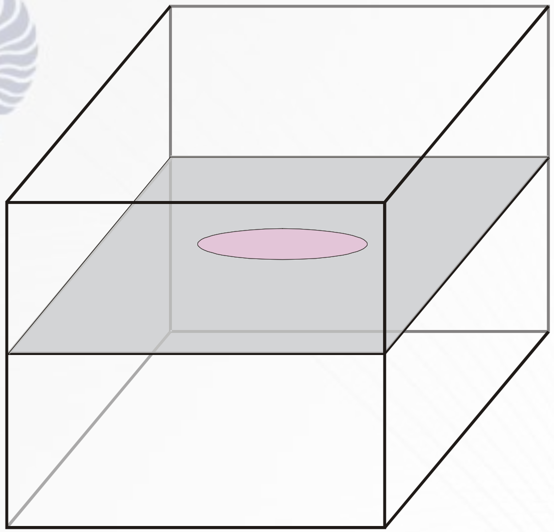
Atomistic mechanism of climb

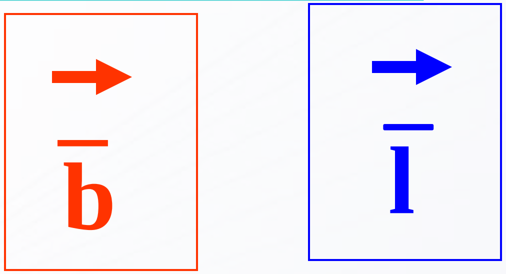


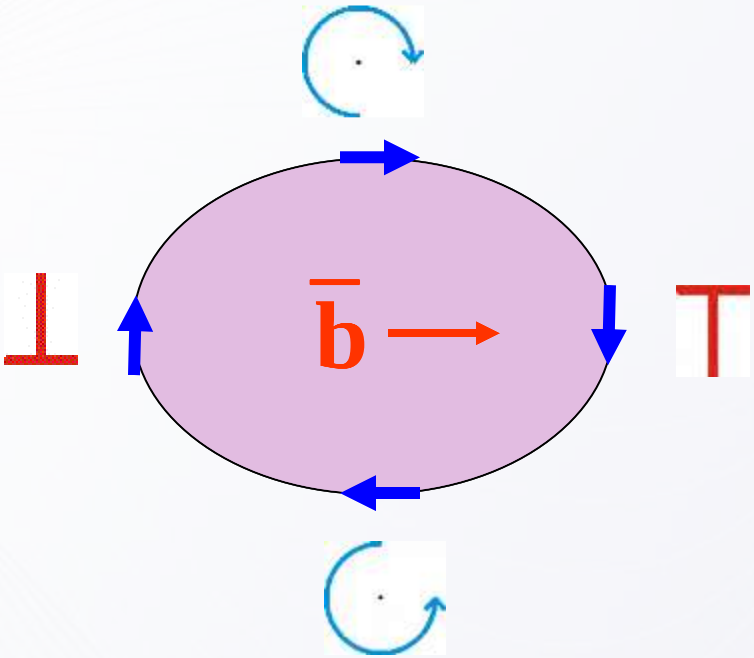
SCREW DISLOCATIONS

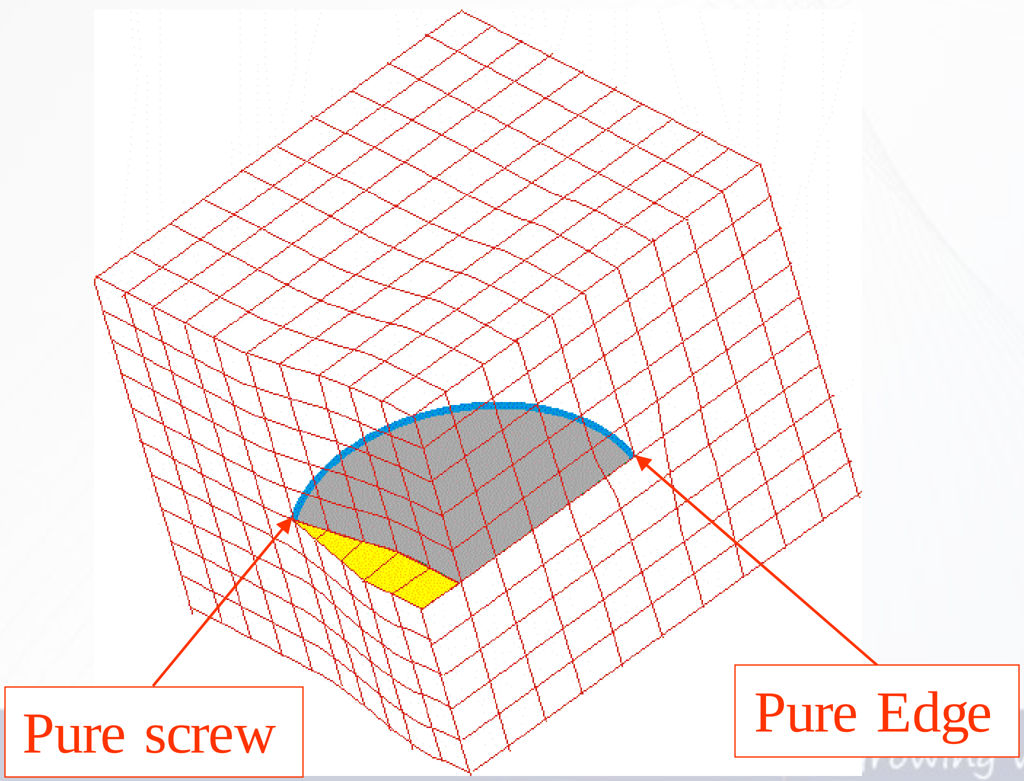


Mixed dislocations





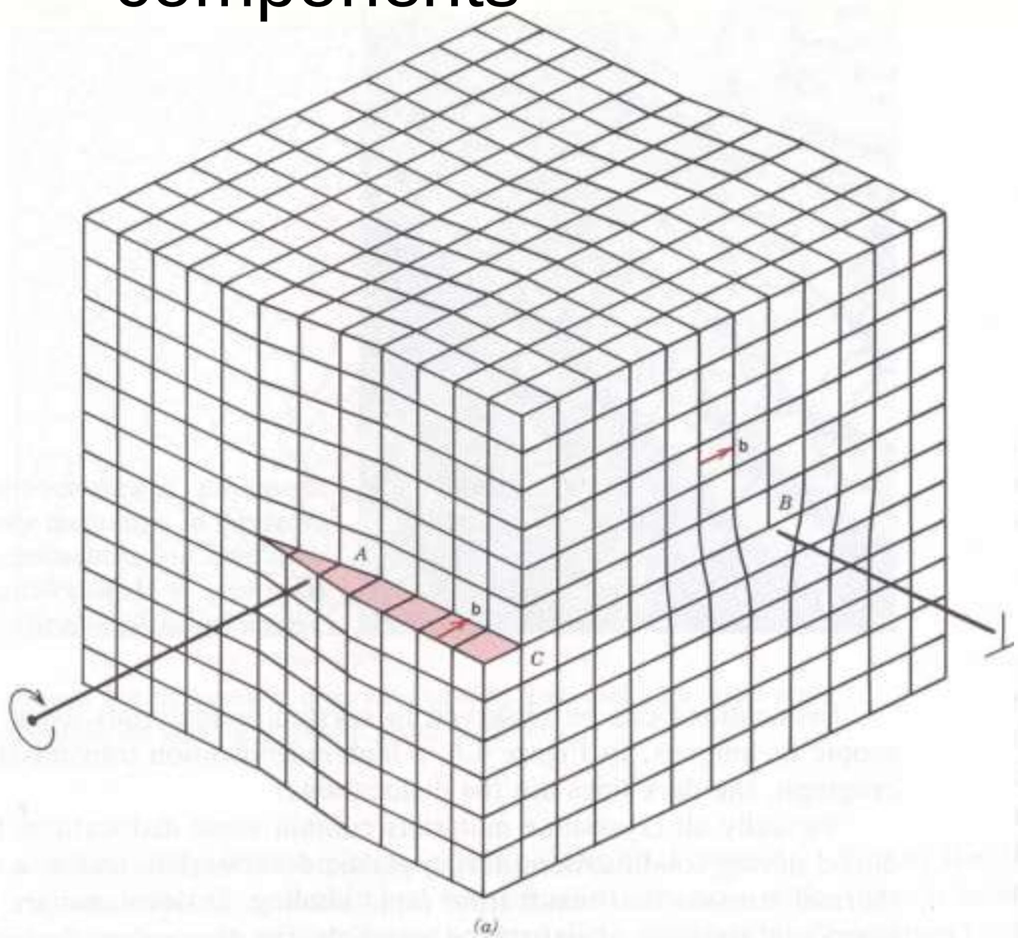




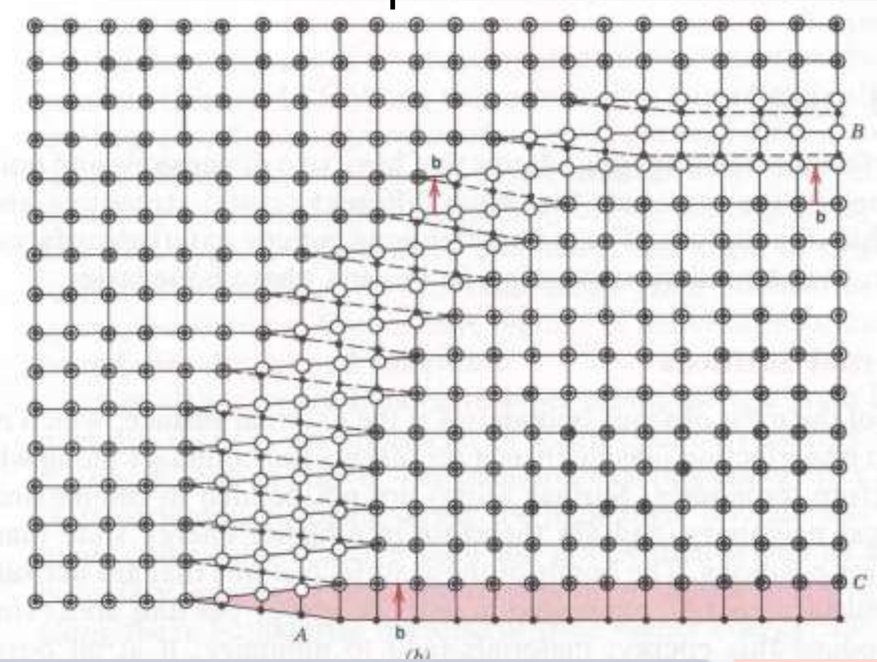
Mixed Dislocations

- ***Mixed dislocations*** have edge & screw components

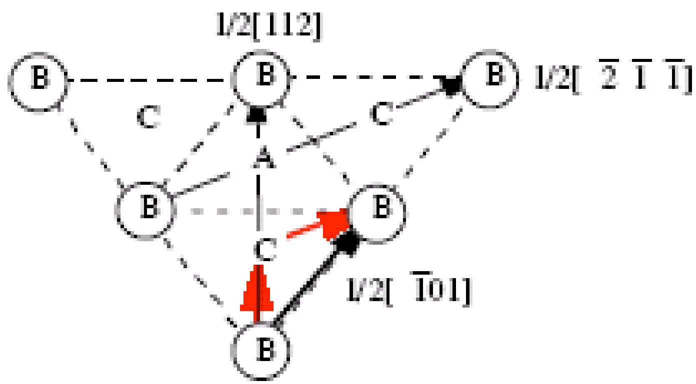
Orientation of line w.r.t. fault vector ***b*** varies along dislocation

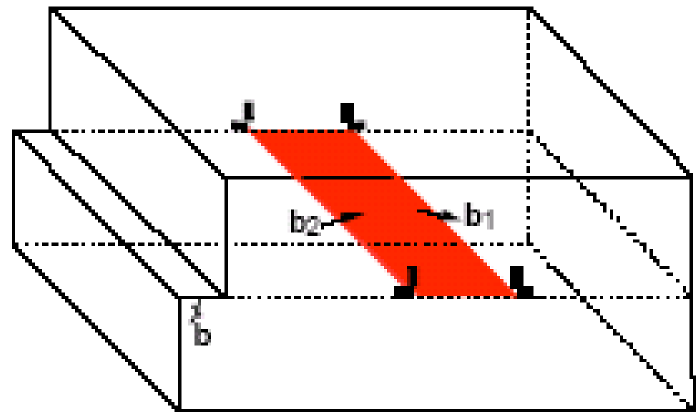


top view



PARTIAL DISLOCATIONS



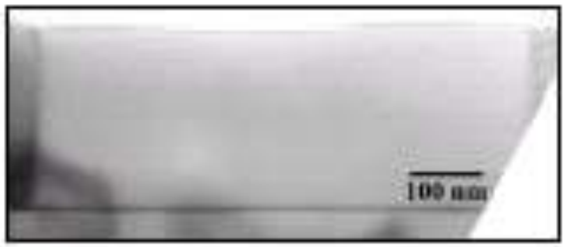


- Sometimes dislocations are split into "partials"
  - Separated by a "stacking fault"
- Common in fcc
  - "Total" dislocation B → B
  - Splits into "partial" dislocations B → C and C → B
  - Separated by "stacking fault" …ABCABC… → …A|CABCA…

Dislocations Created on Indenting Al

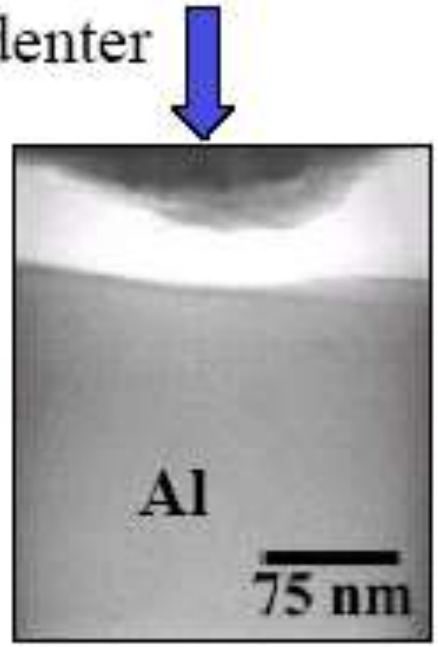
- *Minor, Stach and Morris, Appl. Phys. Lett., 79, 1625-27 (2001)*

Diamond Nanoindenter



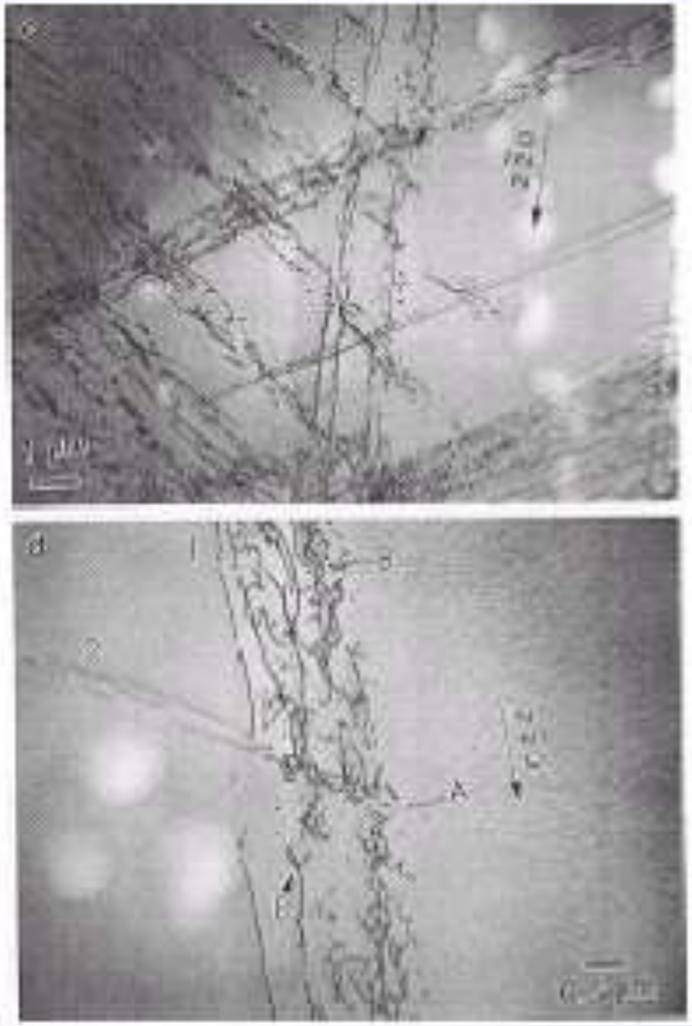
Before

After



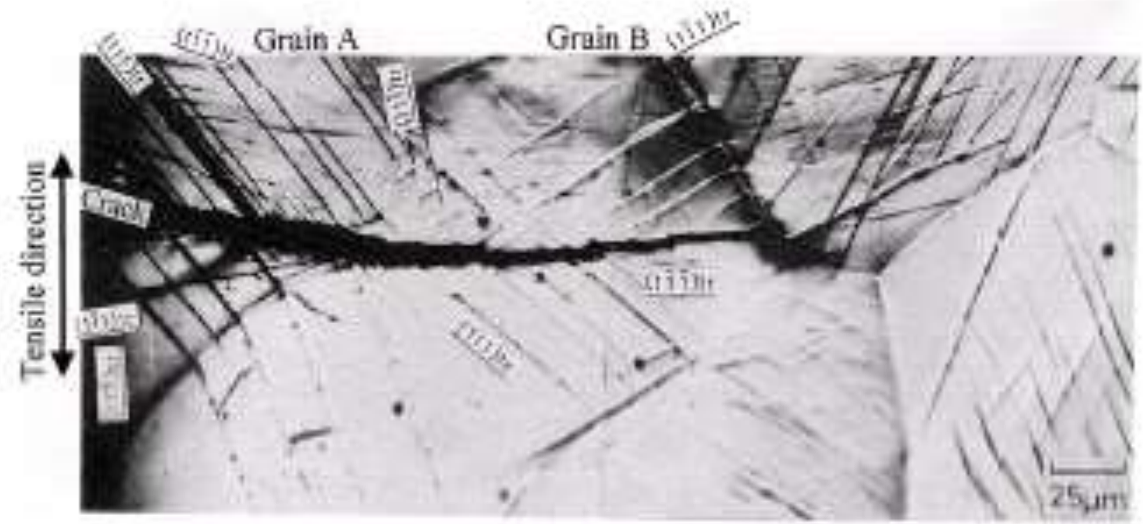
Dislocations in TiC

- Chien, Ning and Heuer, Acta Mater., 44, 2265 (1996)



Slip Lines Across Grains in Stainless Steel

- *Tomota, et al., Acta Mater., 46, 3099-3108 (1998)*



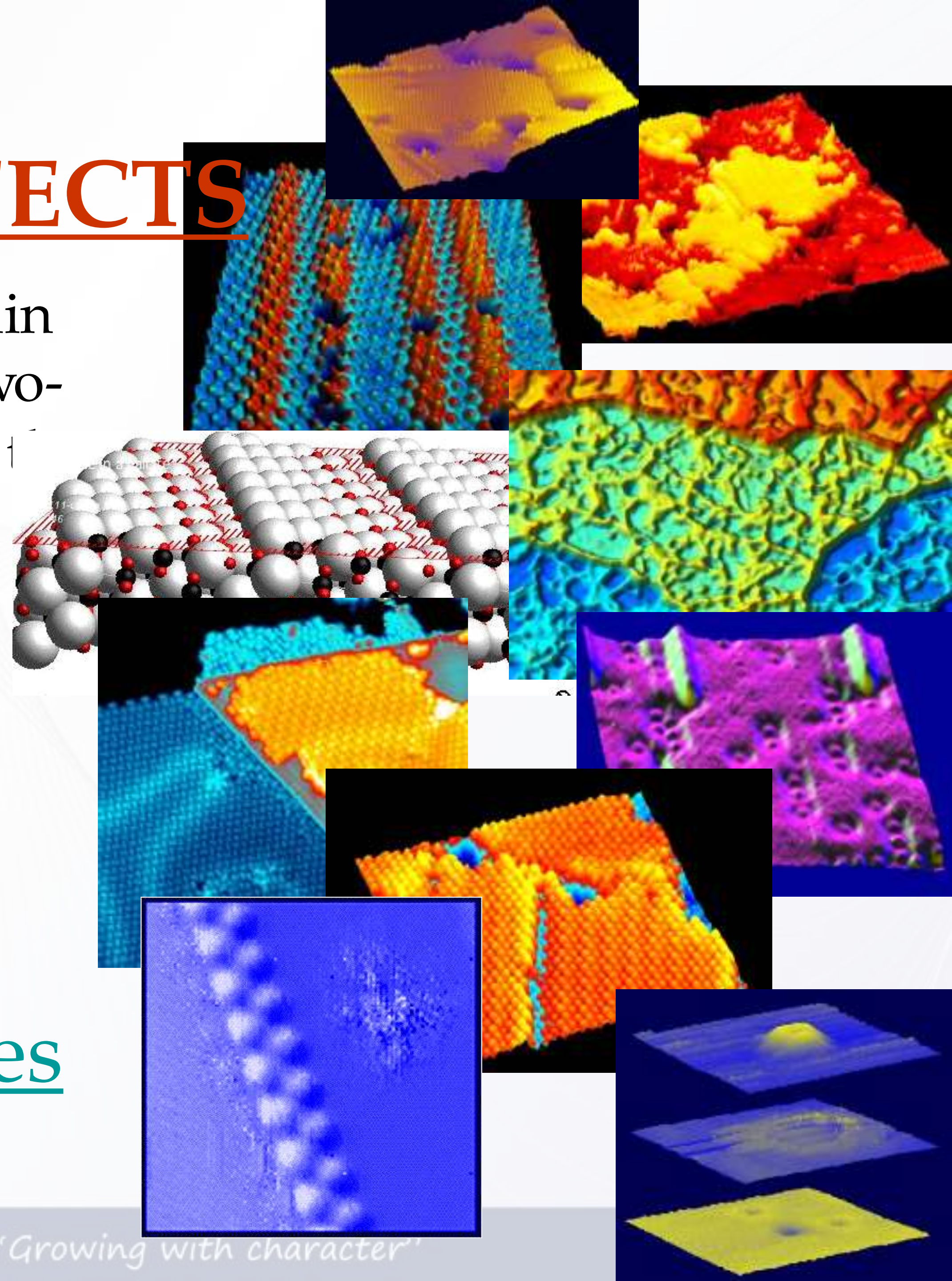
Defects	*Dimensionality*	*Examples*
Point	0	Vacancy
Line	1	Dislocation
Surface	2	Free surface, Grain boundary
Volume	3	Voids, Inclusions, Precipitates

SURFACE DEFECTS

Imperfections, such as grain boundaries, that form a two-dimensional plane within t[he] crystal.

classifications

- free surface
- twin boundary
- stacking faults
- grain boundaries



VOLUME DEFECTS

Three-dimensional defects in solids
Volume defects play an important role in corrosion mechanisms

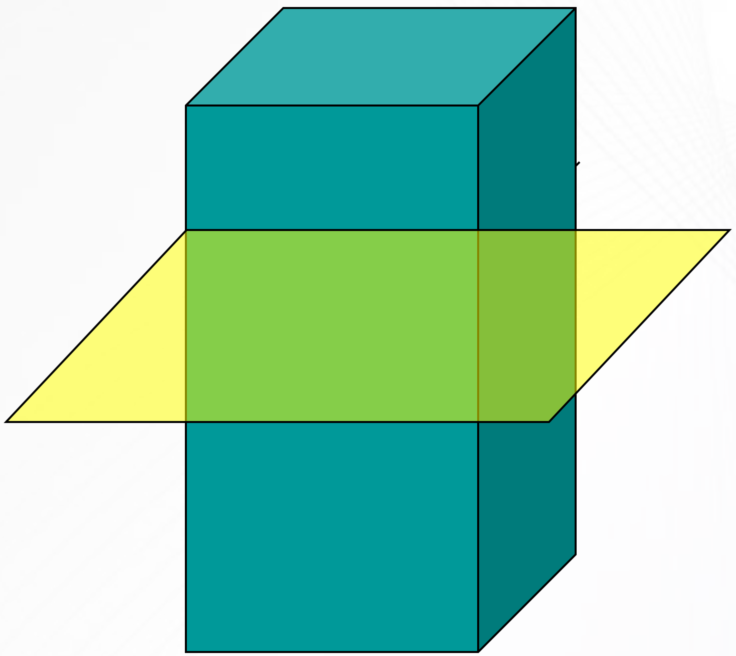
Always involve a second phase
- Porosity (solid – vapor)
- Inclusions (solid – solid)
- Precipitates (solid – solid)
- Cracks (solid – vapor)

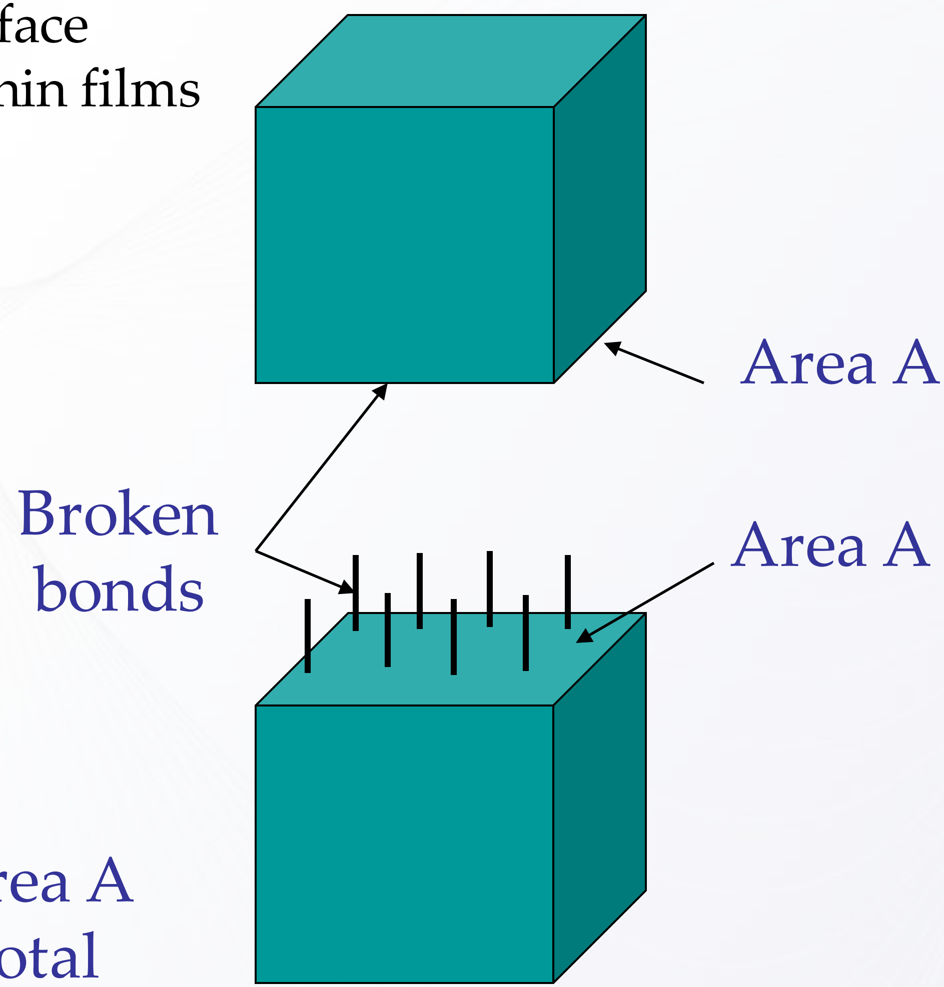
- voids
- inclusions
- precipitates

External	**Internal**	
Free surface	Grain boundary	*Same phase*
	Stacking fault	
	Twin boundary	*Different phases*
	Interphase boundary	

free surface

Surface grooving where grain boundaries intersect free surfaces leads to surface roughness, possibly break-up of thin films





If bond are broken over an area A then two free surfaces of a total area 2A is created

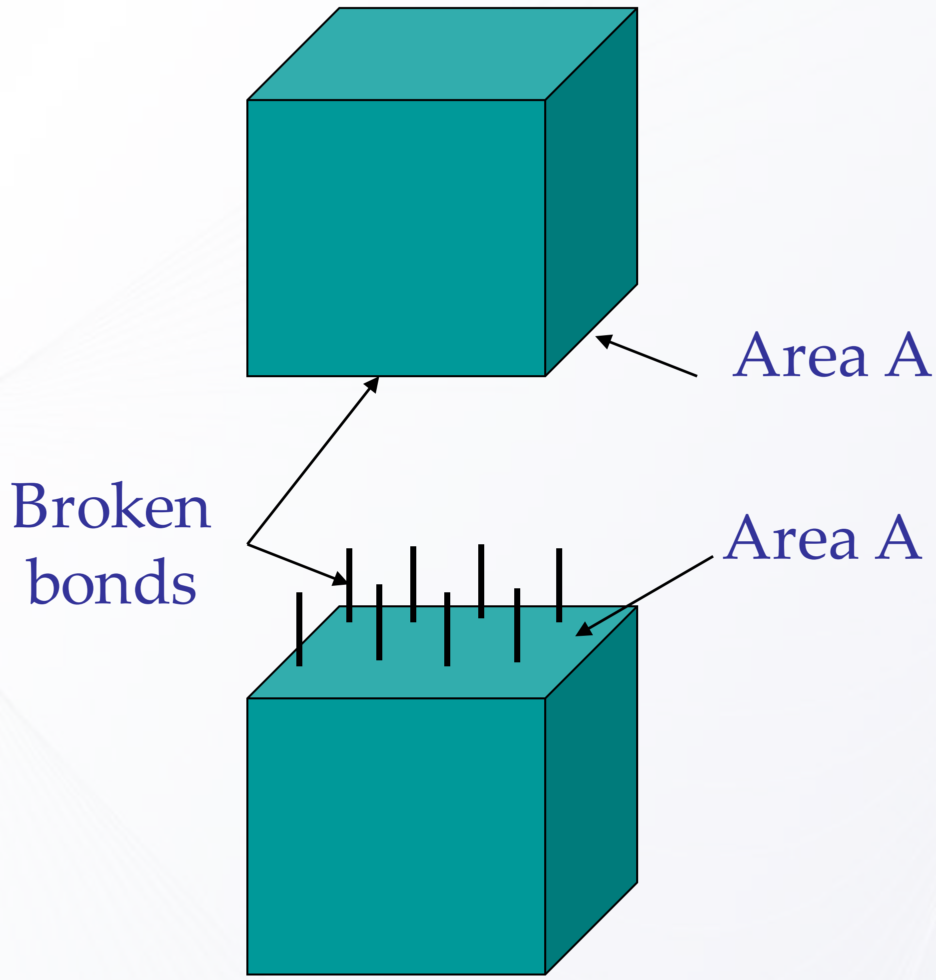
n_A = no. of surface atoms per unit area

n_B = no. of broken bonds per surface atom

ε = bond energy per atom

$$\gamma = \frac{1}{2} n_A n_B \varepsilon$$

Surface energy per unit area

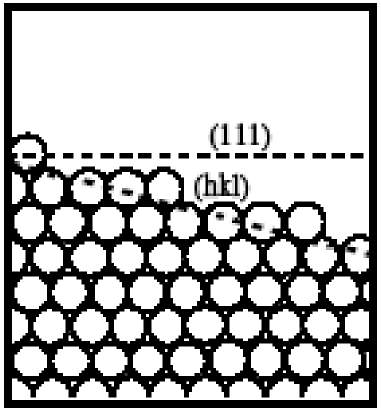


If bond are broken over an area A then two free surfaces of a total area 2A is created

Surface energy is anisotropic

Surface energy depends on the orientation, i.e., the Miller indices of the free surface

n_A, n_B are different for different surfaces

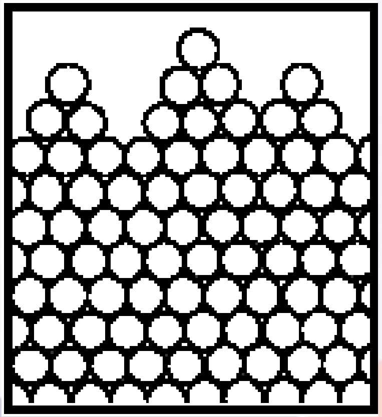


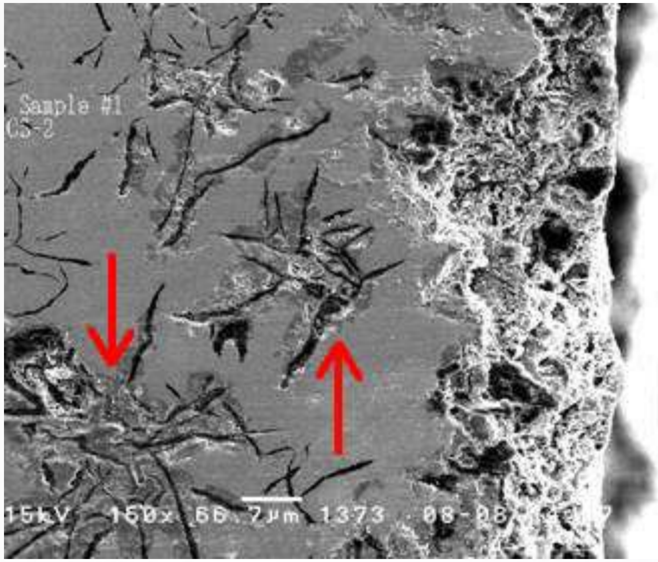
Free Surfaces of Metals

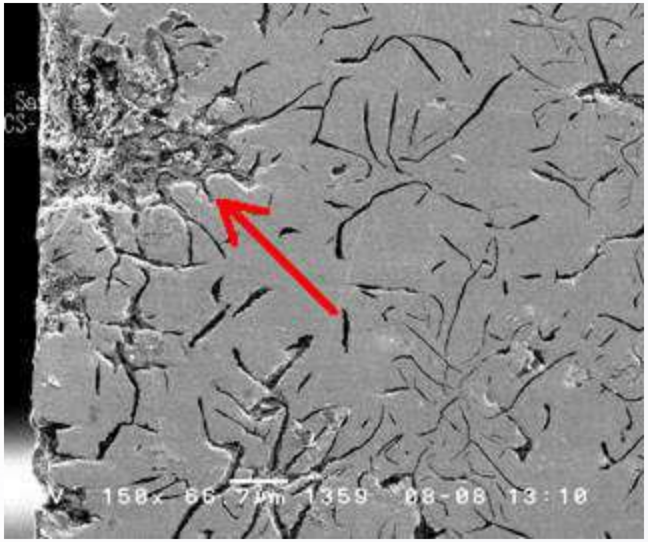
Surface tension (σ) lowest for low-index planes

Diffuse Interface

At high T, metal surfaces tend to be rough, diffuse





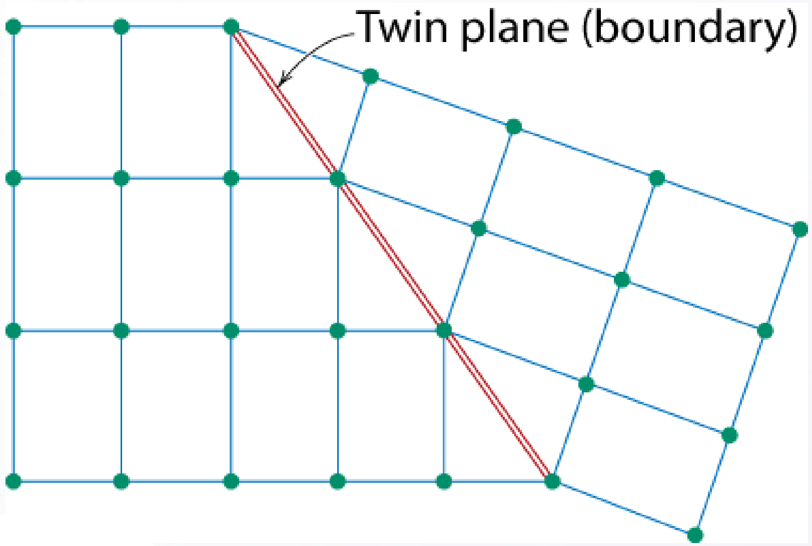


free surface

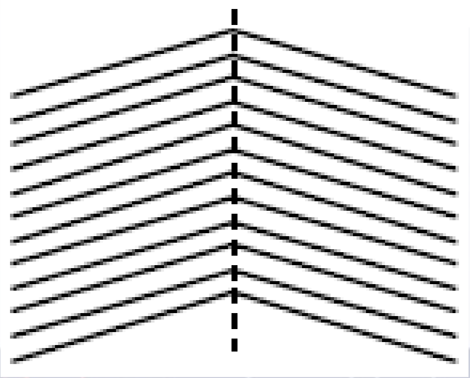
twin boundary (plane)

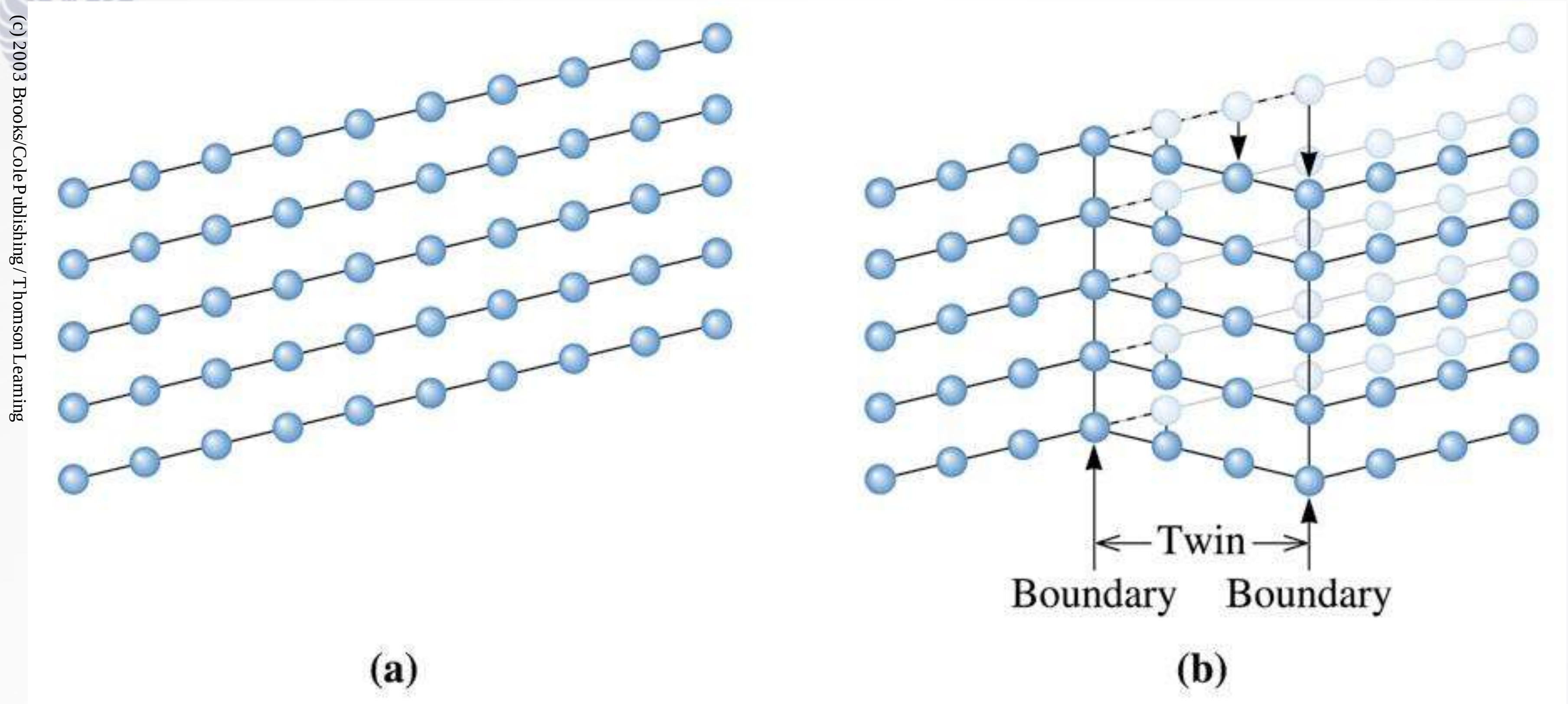
Essentially a reflection of atom positions across the twin plane

Twining is very common in minerals (result of phase transition during cooling)

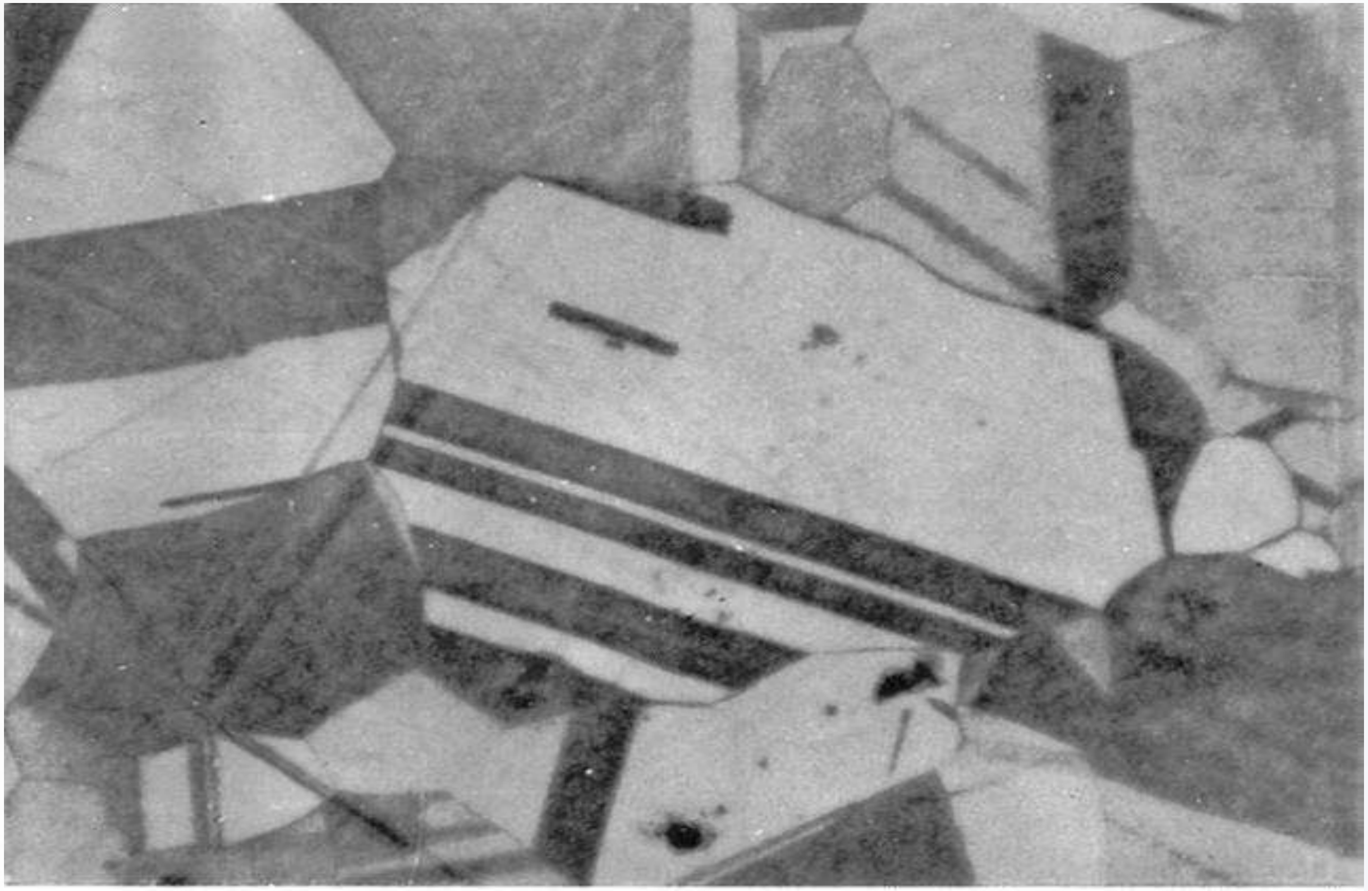


Twinning is an important deformation mechanism
Sn, Mg, high-N austenitic (FCC) steel, Cu at low T





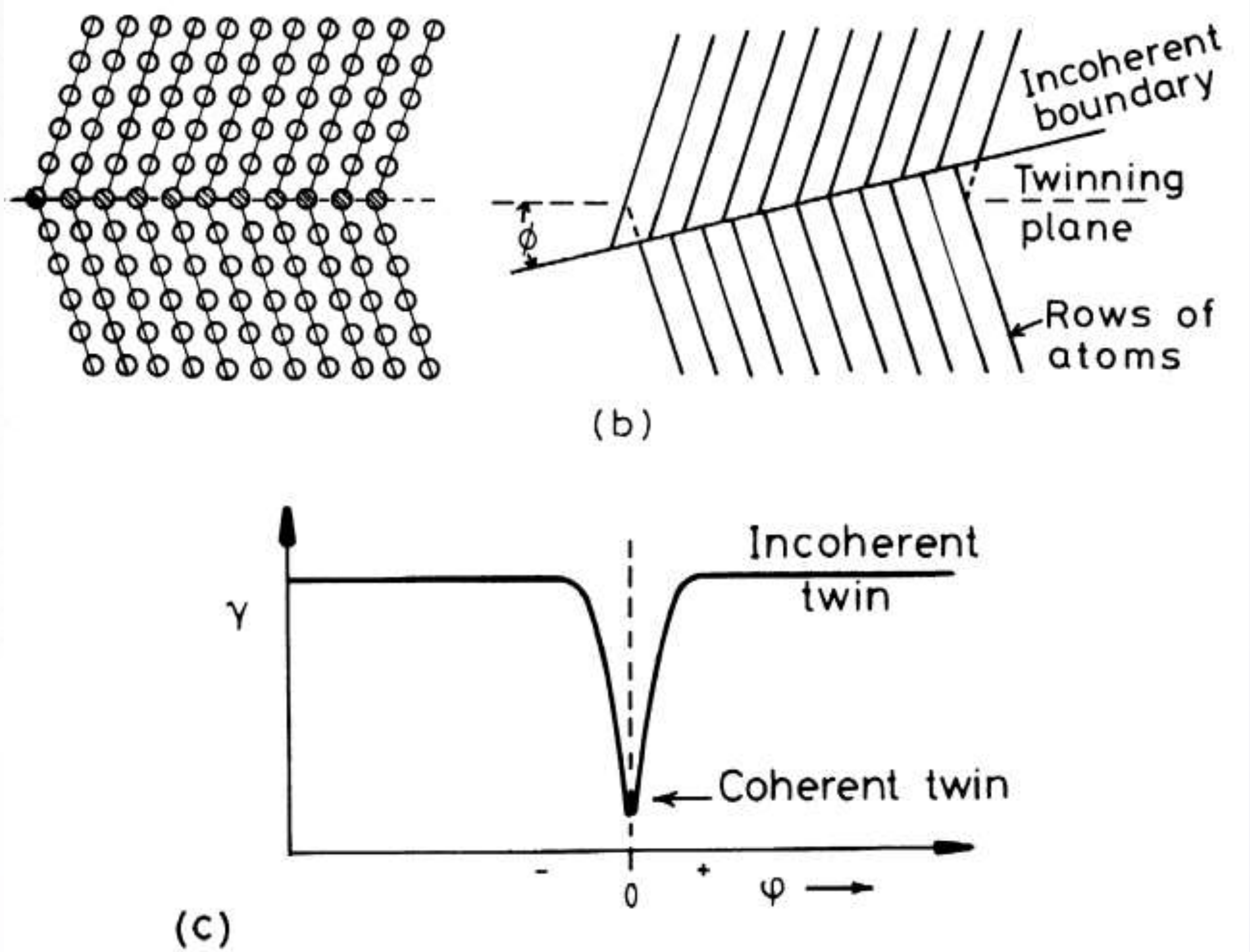
Formation of twin (b) may be caused by application of stress to the perfect crystal (a)



(c)

Figure (c) : A micrograph of twins within a grain of brass (x250)

Twin: coherent vs. incoherent



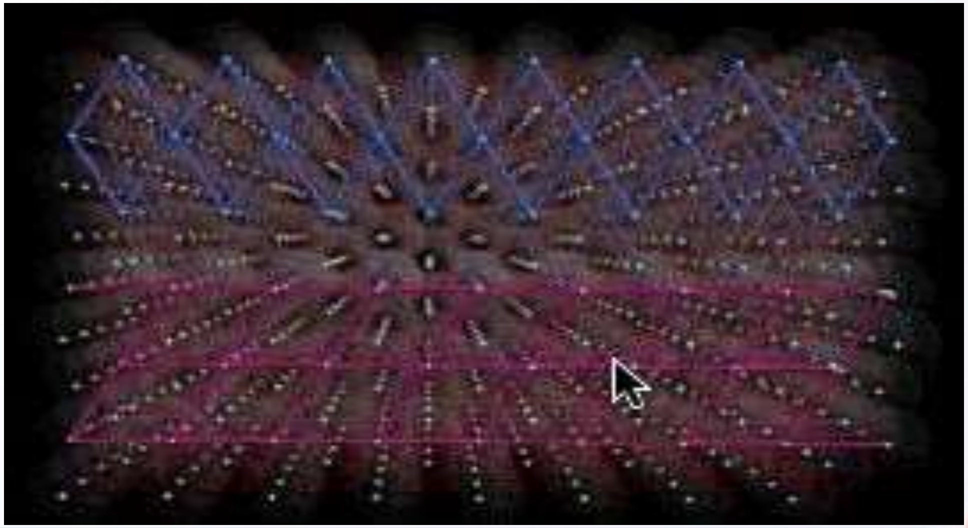
(Porter & Easterling - fig.3.12/p123)

stacking faults

- Stack close-packed planes in wrong sequences
  Create extra or missing plane inside the crystal

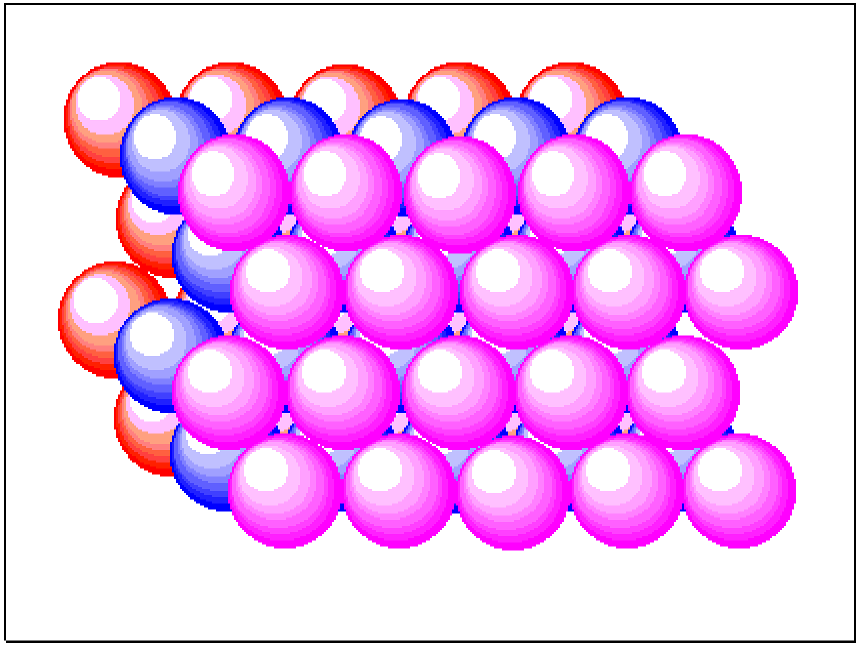
It may occur during

(1) crystallization from the melt or solid state,
(2) solid state processes or recrystallization, phase transition, and crystal growth, and
(3) deformations.



- For FCC metals an error in ABCABC packing sequence

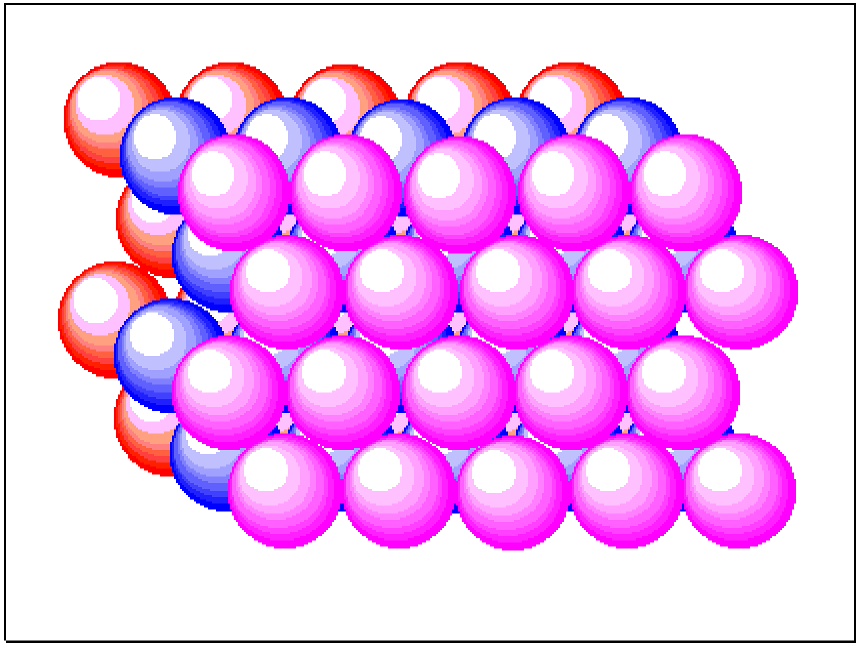
- Intrinsic : Remove a plane (C)
- Extrinsic : Insert an extra plane (A)



ABCABCABC

A	A	A
B	B	B
C	C	C
A	A	A
B	B	B
C	C	C
A	A	A
B	B	B
A	→ C	→ A
B	A	C
C	B	A
A	C	B
B	A	C
C	B	A
A	C	B
B	A	C
C	B	A
	C	B
		C

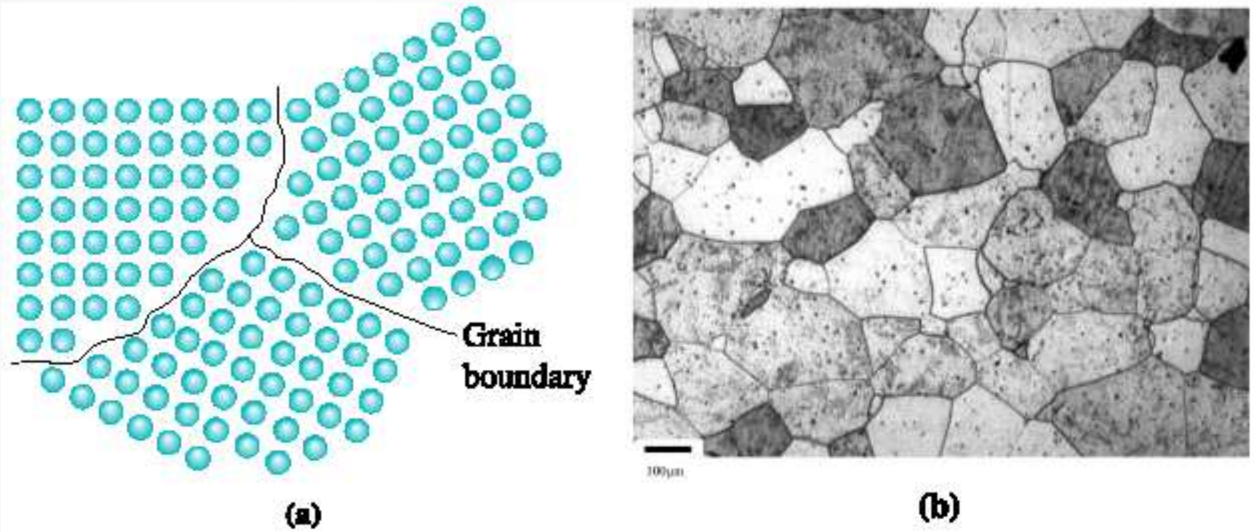
- Intrinsik : menghilangkan bidang C
- Extrinsik : Memasukkan bidang tambahan A
- Kristal sempurna



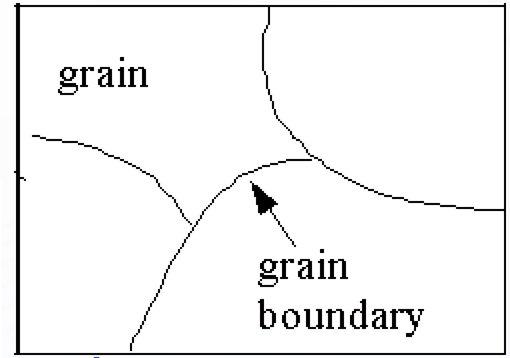
ABCABCABC

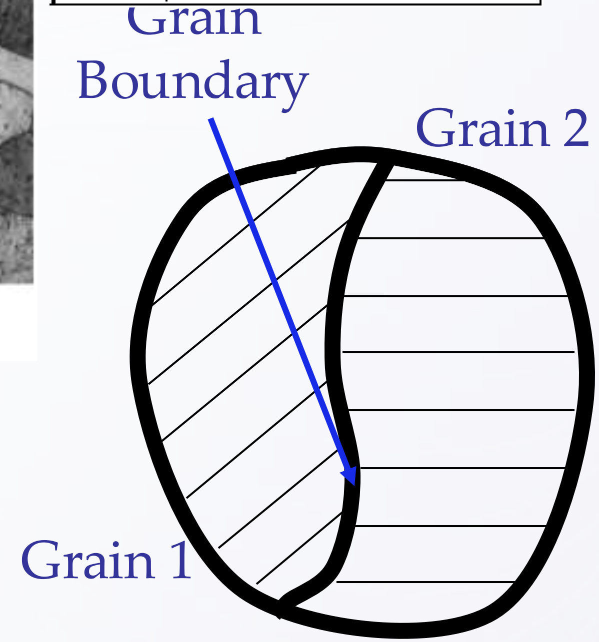
A		A		A
B		B		B
C		C		C
A		A		A
B		B		B
C		C		C
A		A		A
B		B		B
A	→	C	→	A
B		A		C
C		B		A
A		C		B
B		A		C
C		B		A
A		C		B
B		A		C
C		B		A
		C		B
				C

grain boundaries



(a) (b)



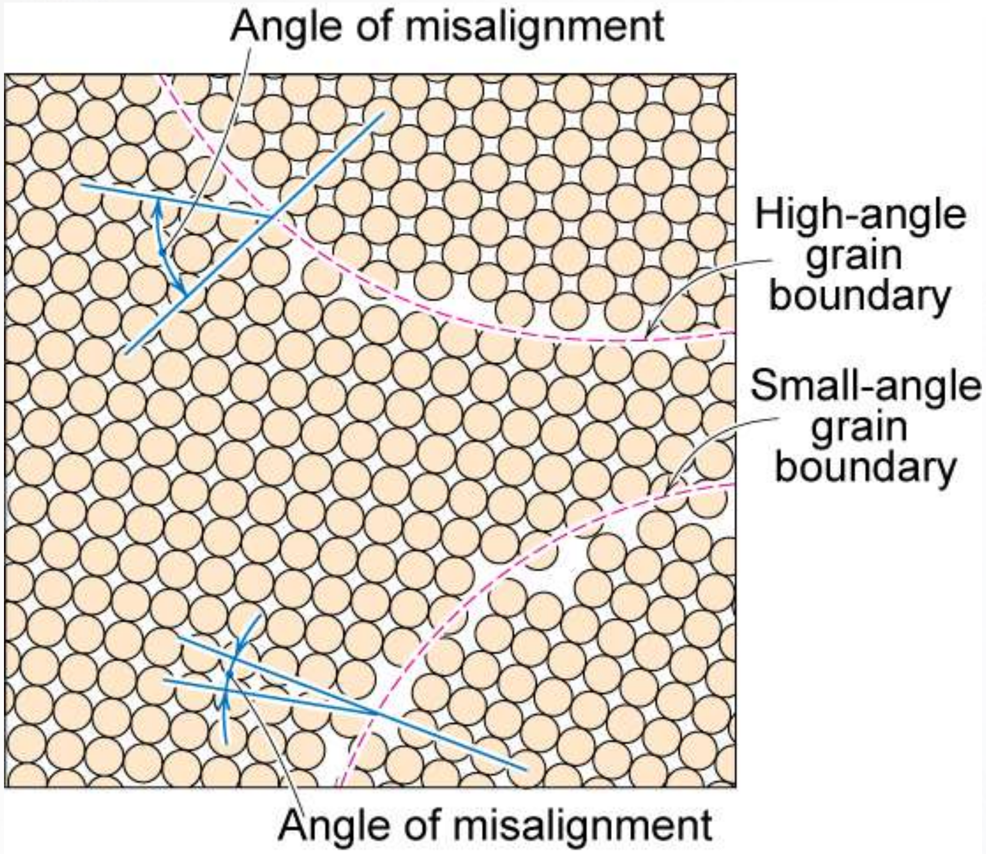


<u>See Figure :</u>

(a) The atoms near the boundaries of the three grains
(b) Grains and grain boundaries in a stainless steel sample.

(*Courtesy Dr. A. Deardo.*)

A grain boundary is a boundary between two regions of identical crystal structure but different orientation



Grains: individual crystals
Grain boundaries: zones between any two grains

- regions between crystals
- transition from lattice of one region to that of the other
- slightly disordered
- low density in grain boundaries
  - high mobility
  - high diffusivity
  - high chemical reactivity

Grain Boundary: *low* and *high angle*

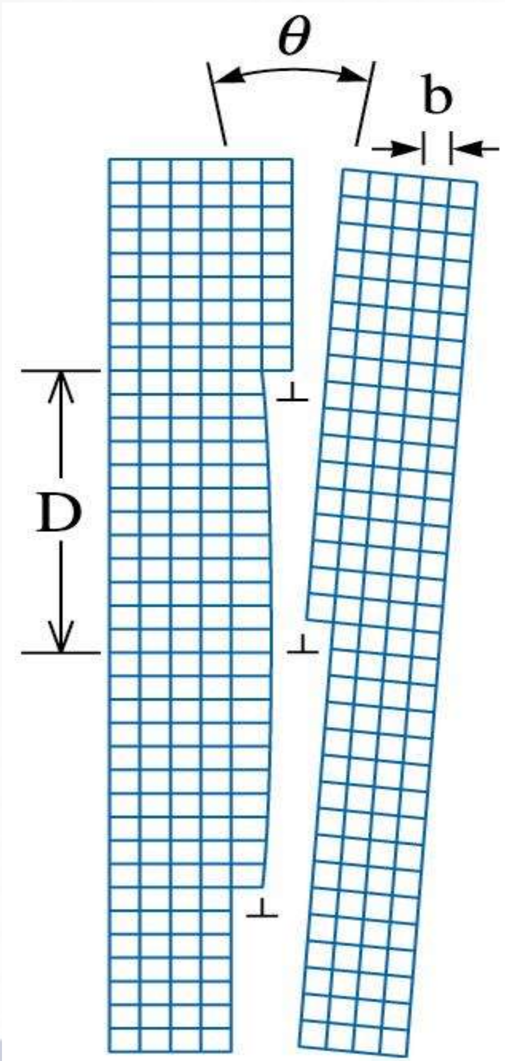
One grain orientation can be obtained by rotation of another grain across the grain boundary about an axis through an **angle**

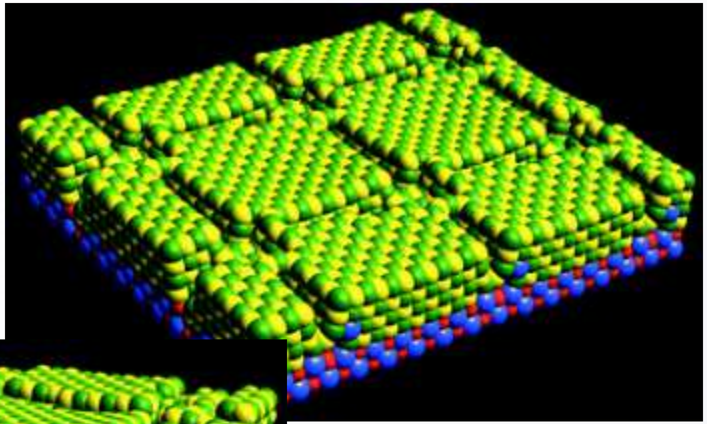
If the angle of rotation is high, it is called a **high angle grain boundary**

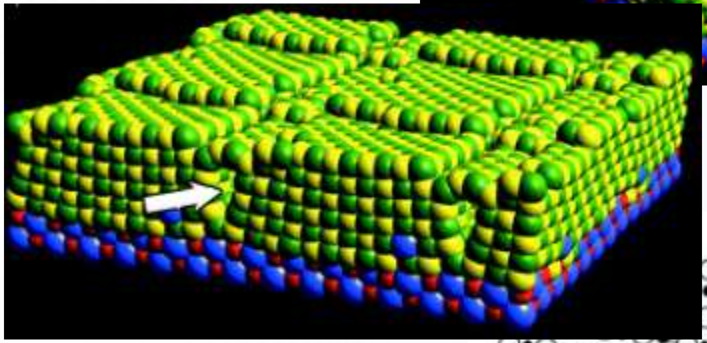
If the angle of rotation is low it is called a **low angle grain boundary**

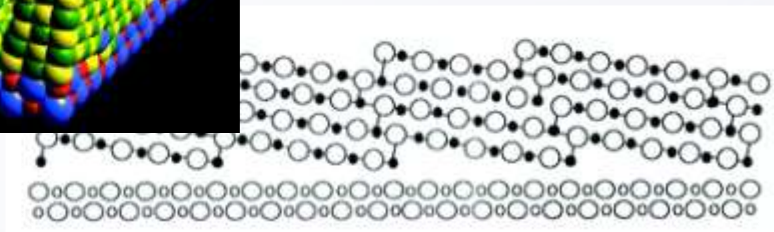
Low-angle grain boundary

- An array of dislocations causing a small misorientation of the crystal across the surface of the imperfection.







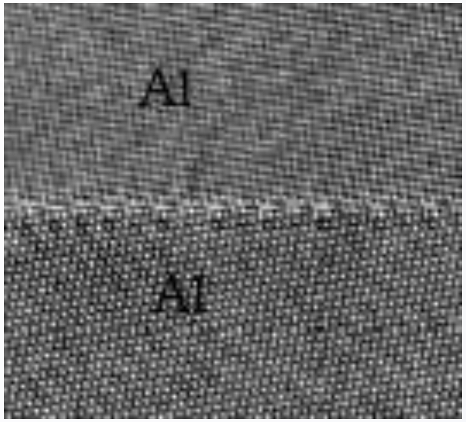


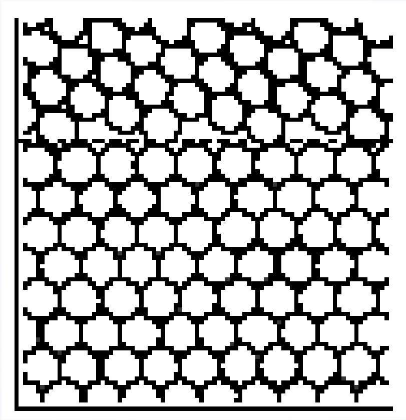
The low angle grain boundary is produced by an array of dislocations, causing an angular mismatch θ between lattices on either side of the boundary.

High-angle grain boundary

High-angle boundaries are likely sites for chemical segregation

A simple high-angle boundary where two crystals meet





Grain Boundary: *tilt* and *twist*

One grain orientation can be obtained by rotation of another grain across the grain boundary about an **axis** through an angle

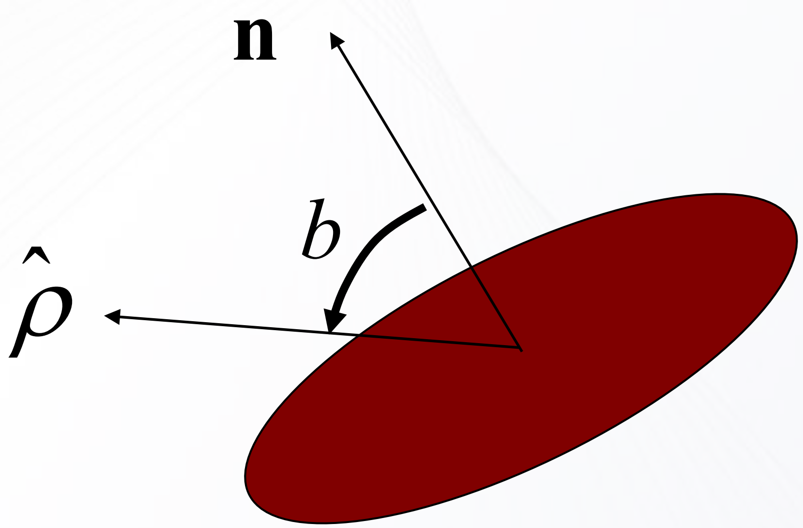
If the axis of rotation lies in the boundary plane it is called **tilt boundary**

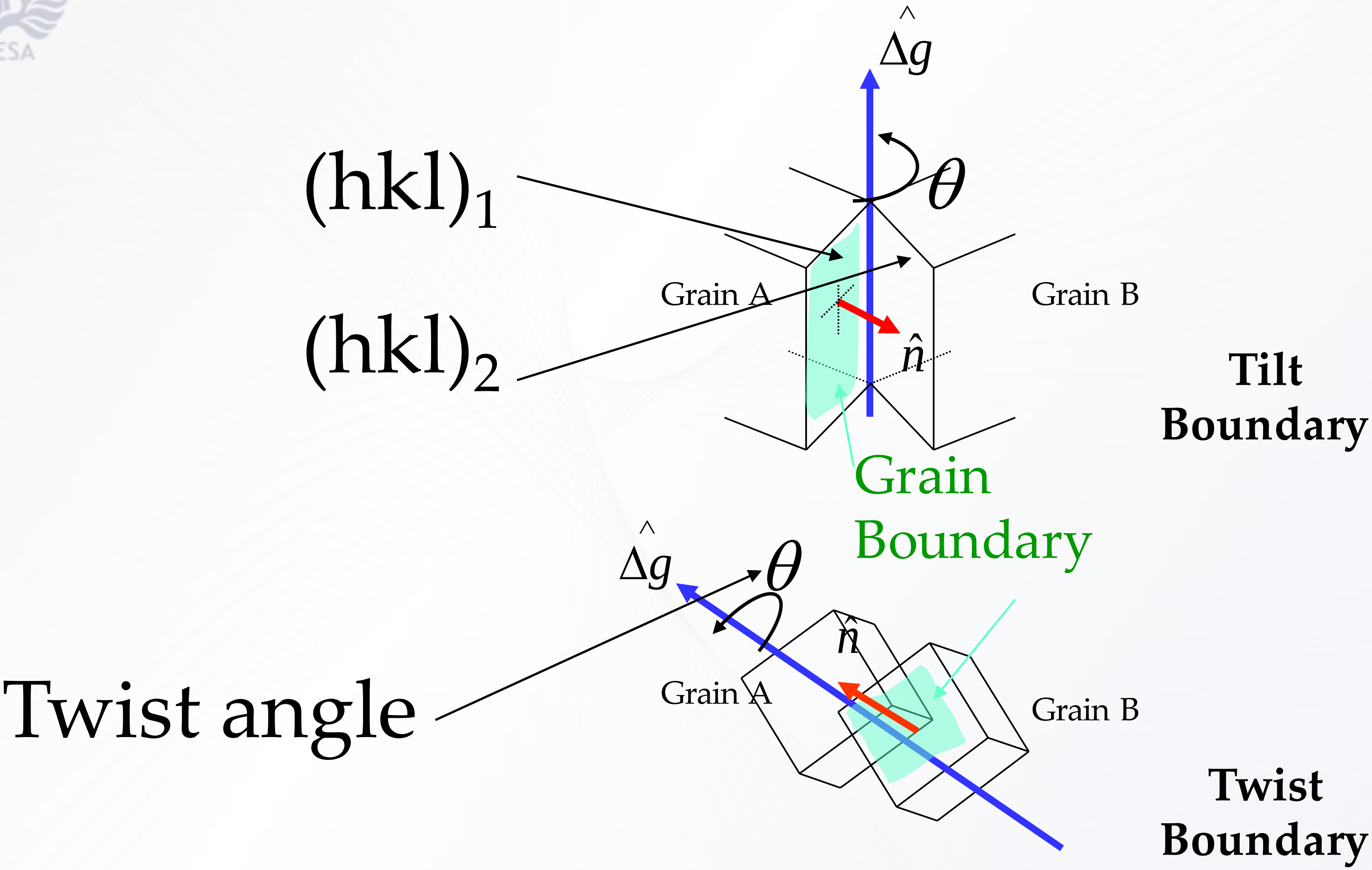
If the angle of rotation is perpendicular to the boundary plane it is called a **twist boundary**

Tilt-twist character

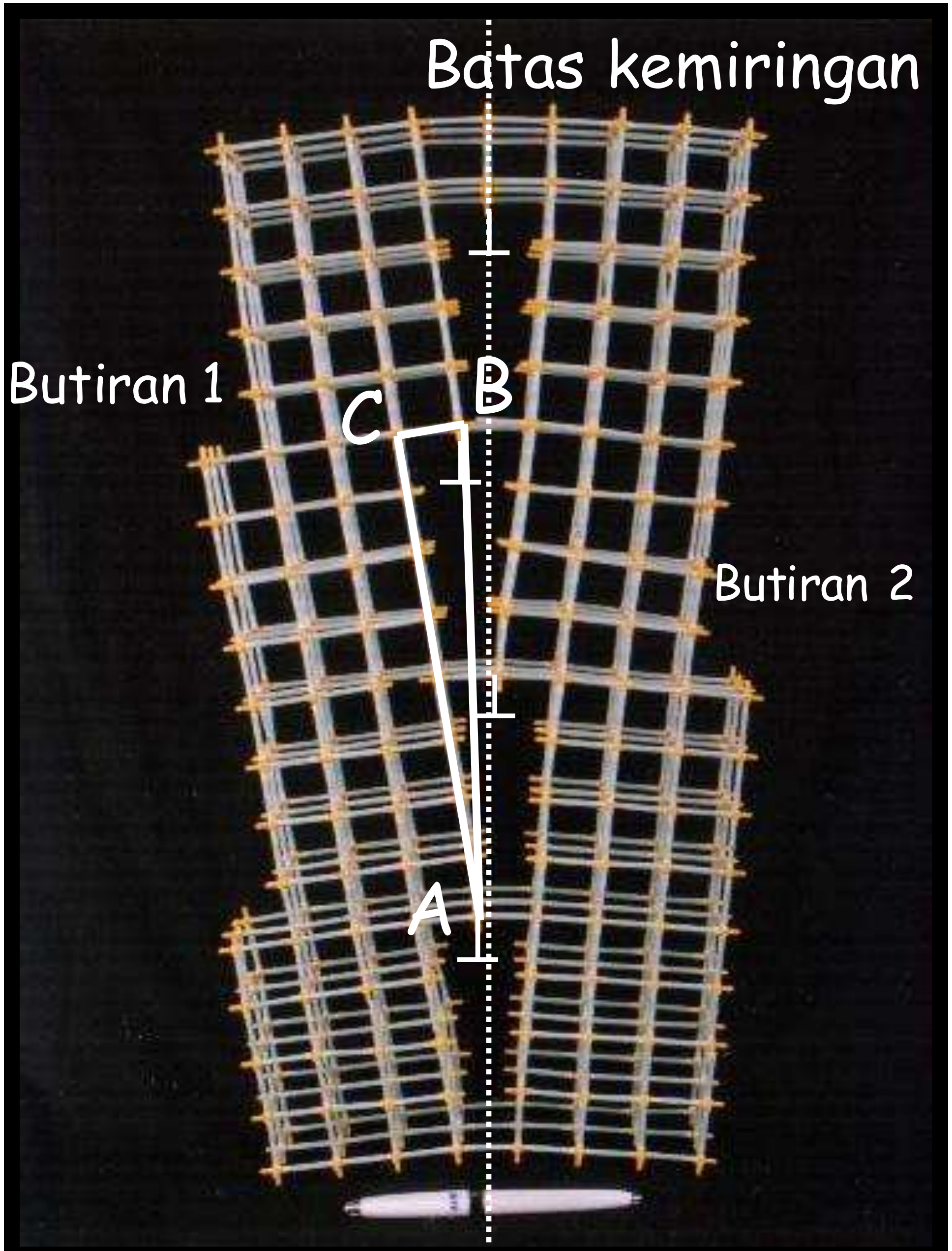
If $\cos^{-1}(b)=0°$, boundary is pure twist;

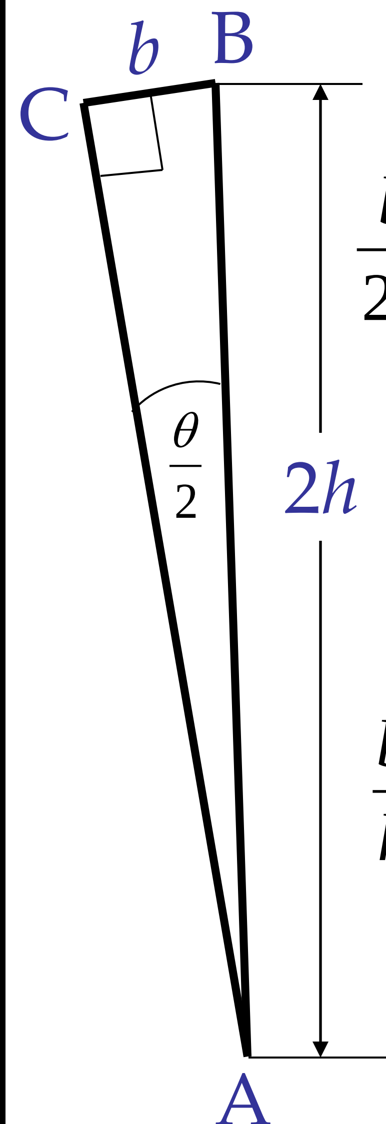
If $\cos^{-1}(b)=90°$, boundary is pure tilt.





$\hat{\Delta g}$
θ
$(hkl)_1$
$(hkl)_2$
Grain A
Grain B
$\hat{n}$
Tilt Boundary
Grain Boundary
$\hat{\Delta g}$
θ
$\hat{n}$
Twist angle
Grain A
Grain B
Twist Boundary



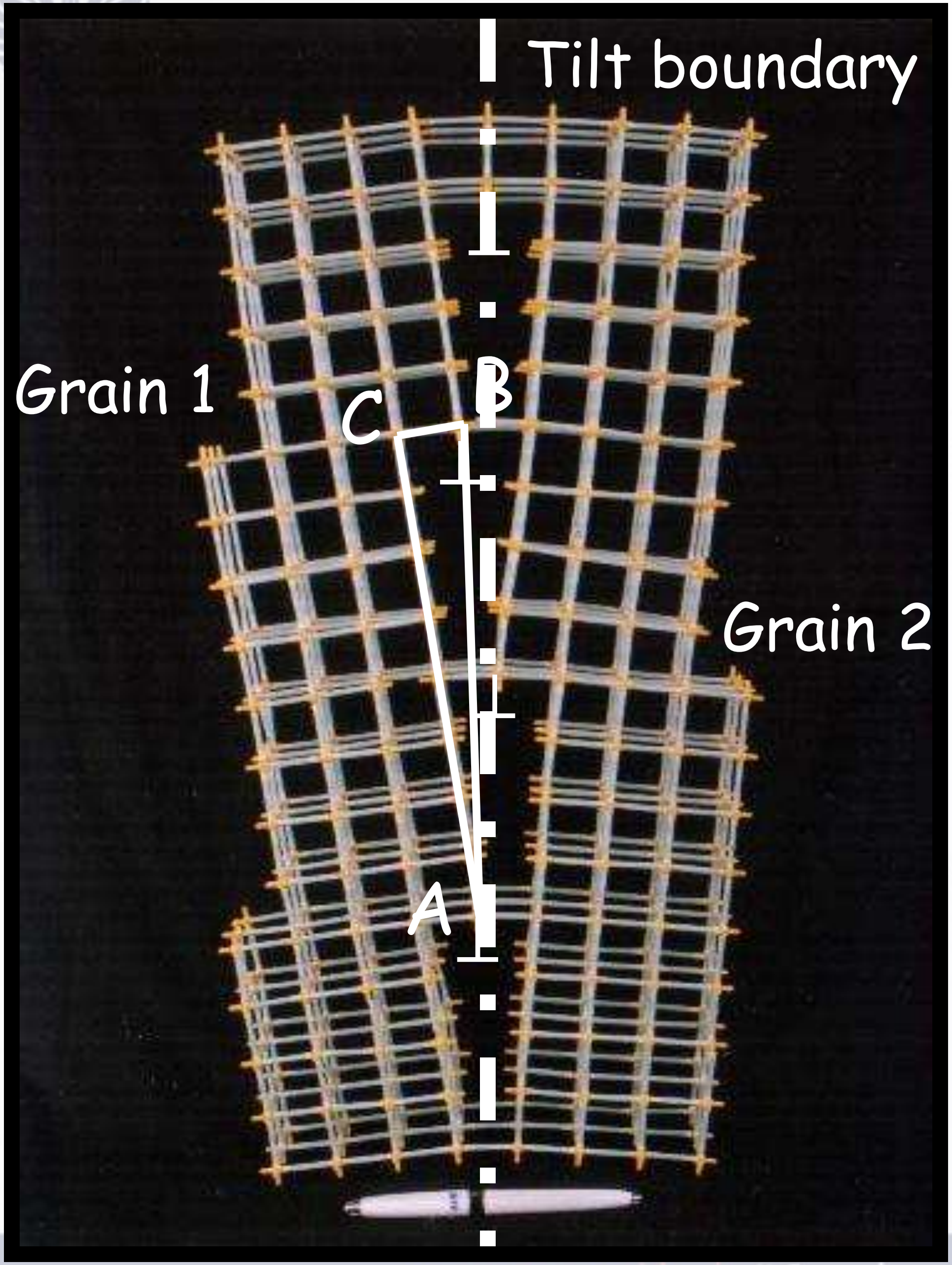


$$\frac{b}{2h} = \sin\frac{\theta}{2}$$

Atau

$$\frac{b}{h} = \tan\theta$$

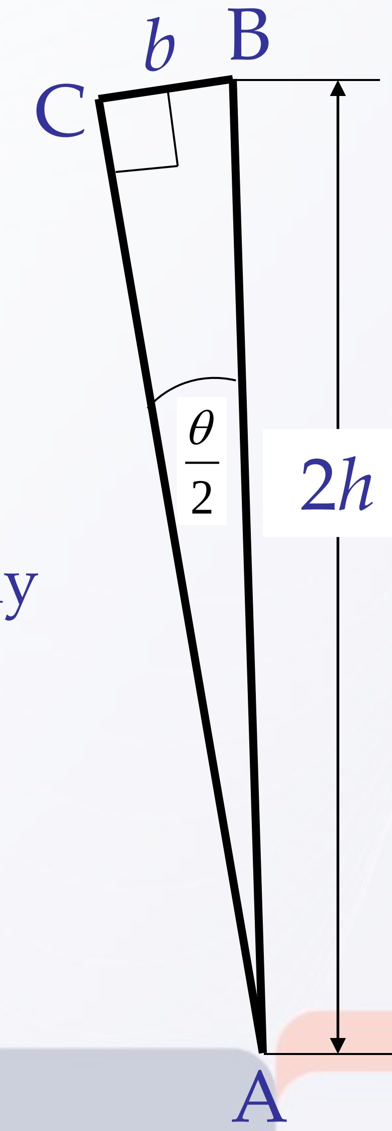
Edge dislocation model of a small angle tilt boundary



$$\frac{b}{2h} = \sin\frac{\theta}{2}$$

Or approximately

$$\frac{b}{h} = \tan\theta$$



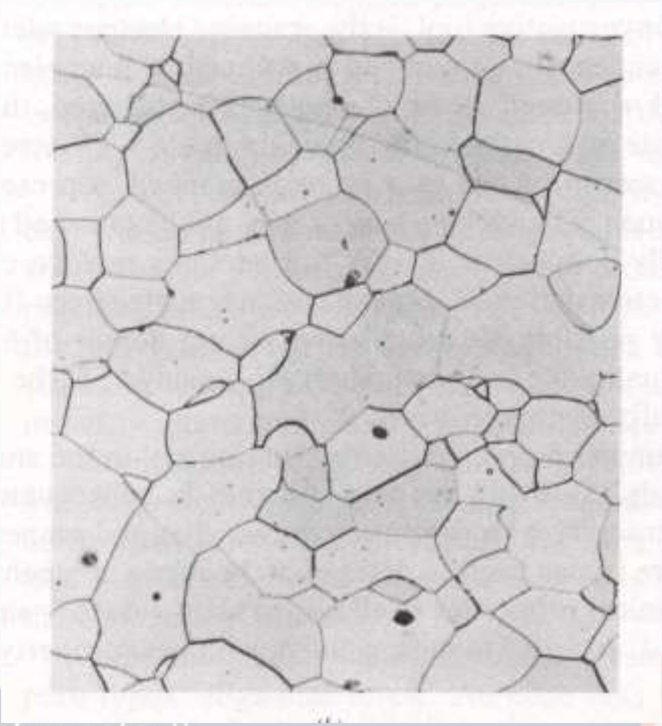
voids (porosity)

- holes in the materials

Voids are small regions where there are no atoms, and can be thought of as clusters of vacancies

inclusions

inclusions particles of foreign matter embedded in the solid



precipitations

Every impurity introduced into a crystal has a certain level of solubility, which defines the concentration of that impurity that the solid solution of the host crystal can accommodate.

Impurity solubility usually decreases with decreasing temperature.

If an impurity is introduced into a crystal at the maximum concentration allowed by its solubility at a high temperature,

↓

the crystal will become supersaturated with that impurity once it is cooled down.

↓

A crystal under such supersaturated conditions seeks and achieves equilibrium by **precipitating** the excess impurity atoms into another phase of different composition or structure.

↓

PRECIPITATES

Impurities cluster together to form small regions of a different phase

Precipitates are considered undesirable because they have been known to act as sites for the generation of dislocations

Precipitates induced during silicon wafer processing come from oxygen, metallic impurities, and dopants like boron

Importance of Defects

- Effect on Mechanical Properties via Control of the Slip Process
- Strain Hardening
- Solid-Solution Strengthening
- Grain-Size Strengthening
- Effects on Electrical, Optical, and Magnetic Properties

Defectoscope

Defectoscope

Detect fine surface defects

The system can detect flaws as fine as 30 microns on polished surfaces

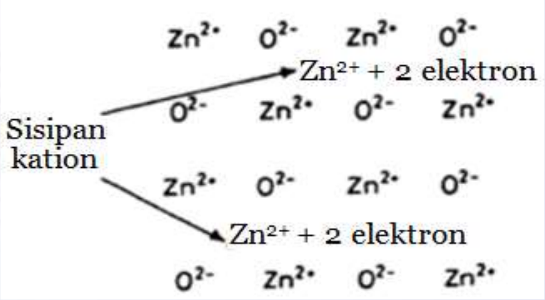
Electron microscopy

Optical microscopy

- Selain diklasifikasikan berdasarkan dimensinya, cacat kristal juga diklasifikasikan berdasarkan stoikiometriknya.
- Berdasarkan stoikiometriknya, cacat kristal dibagi menjadi dua katagori, yaitu cacat stoikiometrik dan cacat nonstoikiometrik.
- Cacat stoikiometrik diakibatkan faktor temperatur sehingga atom/ion pindah meninggalkan posisi normalnya menghasilkan cacat kekosongan & / cacat sisipan ➔ tidak mengubah rumus kimia suatu senyawa
- Cacat nonstoikiometrik diakibatkan oleh sebagian kecil atom hilang atau ketambahan atom pengotor ke dalam kisi yang tidak sempurna ➔ dapat mengubah rumus kimia suatu senyawa. Contoh $NaCl_{0,95}$

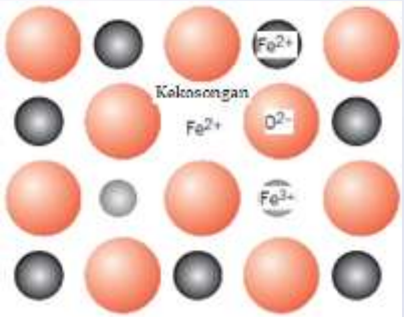
Cacat kristal nonstokiometrik dibagi menjadi tiga:

1. Cacat kelebihan logam / cacat pusat *F* / cacat pusat warna

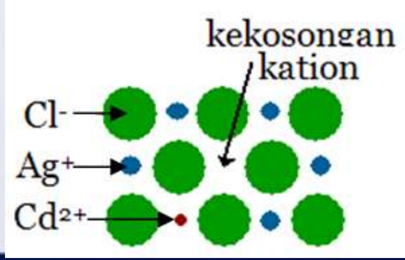


Cacat kelebihan logam pada $Zn_{1+x}O$

2. Cacat kekurangan logam

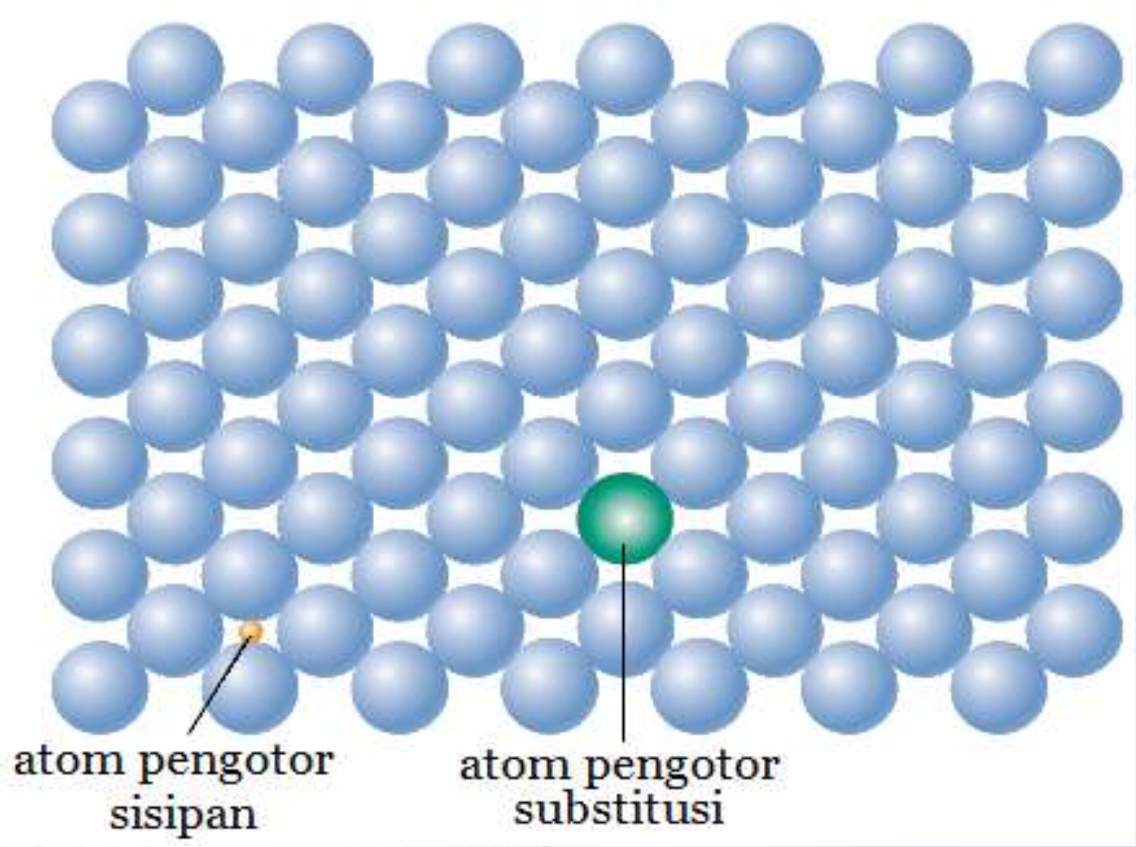


3. Cacat ketidakmurnian (*Impurity defect*)



Larutan padat (*solid solution*)

- Larutan padat adalah campuran homogen berwujud padat yang terdiri dari satu atau lebih zat terlarut dalam pelarut.
- Pelarut (*solvent*) mewakili unsur atau senyawa yang ada dalam jumlah terbesar. Terkadang, atom pelarut juga disebut atom *host*.
- Zat terlarut (*solute*) digunakan untuk menunjukkan unsur atau senyawa yang ada dalam konsentrasi kecil.



Gambar. Atom pengotor sisipan dan substitusi pada larutan padat

Cacat titik ketidakmurniaan ditemukan pada larutan padat, dimana ada dua jenis: substitusi dan sisipan. Untuk jenis substitusional, atom terlarut atau pengotor menggantikan atom pelarut

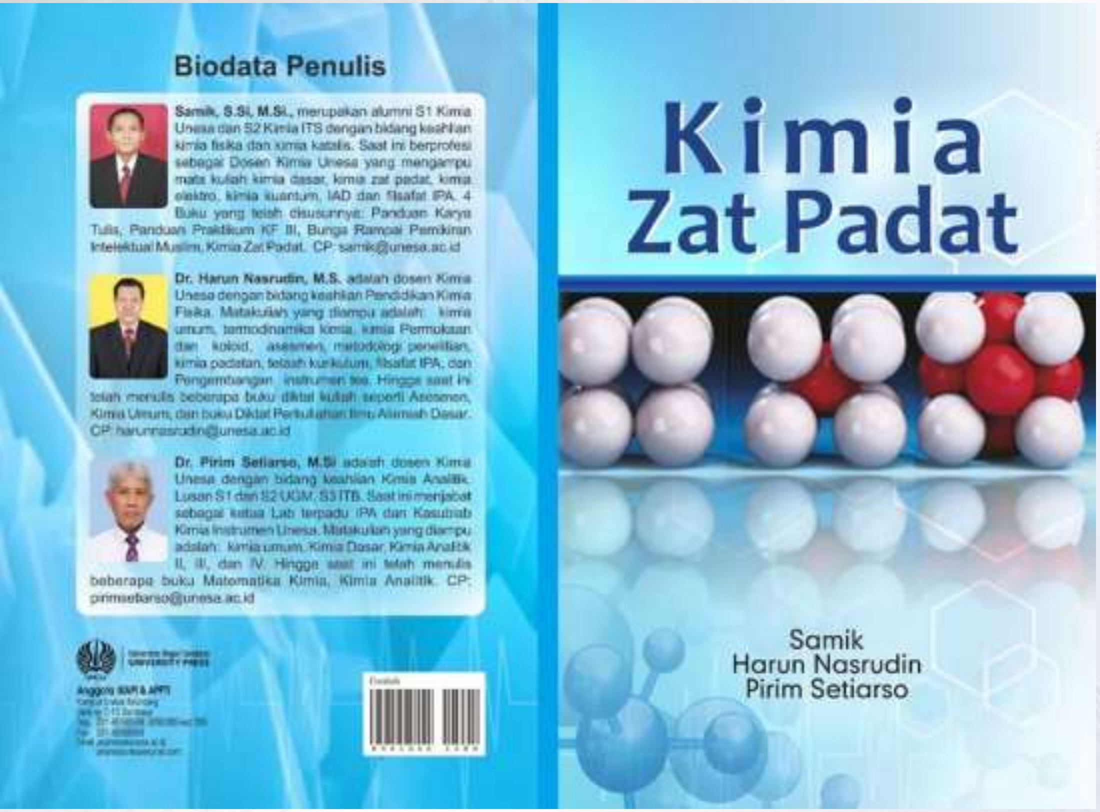
Jawablah soal-soal berikut dengan benar!

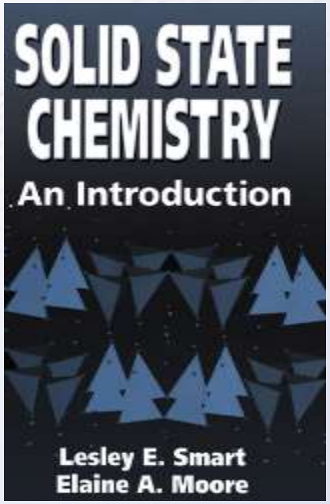
1. Tuliskan macam-macam cacat kristal berdasarkan dimensinya!
2. Kenapa besi oksida (FeO) dapat mengalami cacat kekurangan logam?
3. Bagaimana cara membuat kristal NaCl yang mengalami cacat kelebihan logam?
4. Apa yang dimaksud larutan padat?
5. Apa perbedaan larutan padat substitusional dan larutan padat sisipan?
6. Apa perbedaan Cacat Frenkel dengan cacat Schottky?
7. Tuliskan macam-macam cacat kristal nonstokiometrik!
8. Untuk kristal KCl dan KI, manakah yang lebih mudah mengalami a) Cacat Frenkel; b) Cacat Schottky

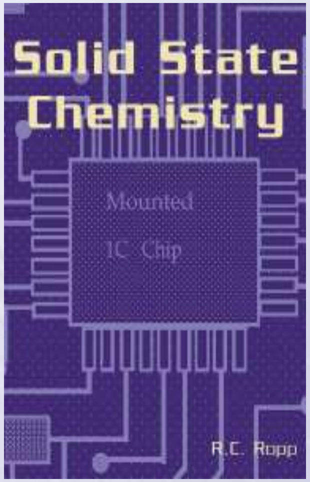
UNESA

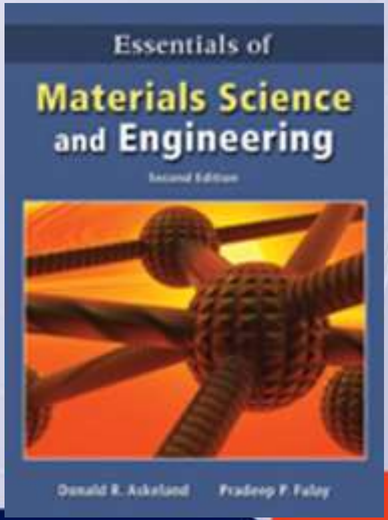
Referensi

Buku ajar kimia zat padat,
buku referensi lainnya, artikel ilmiah dll

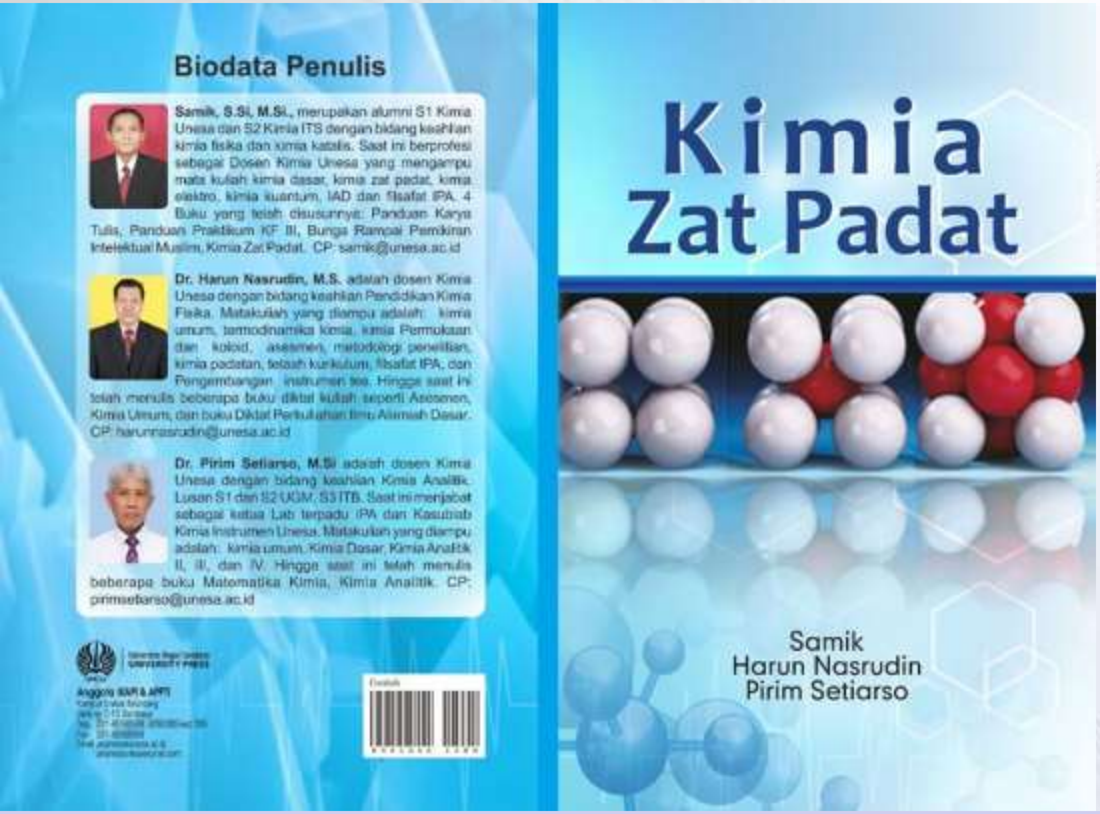








Untuk lebih memahami materi ini silahkan baca di buku kami / yg lain:



PPT ini digunakan untuk mempermudah pembelajaran, kebanyakan saya ambil dari berbagai literatur buku dan PPT (terutama yg berbahasa Inggris) dan dari buku Kimia Zat Padat, Samik dkk.

Mau ebook buku Kimia Zat Padat, silahkan klik https://bit.ly/ebookKZP / 085731160005

Daftar Isi buku Kimia Zat Padat, Mau ebooknya, silahkan klik https://bit.ly/ebukuKZP / 085731160005

DAFTAR ISI

TERIMAKASIH